INSTITUTE NOTES.

APRIL 1939.

FORTHCOMING MEETINGS.

SUMMER MEETING.

The Summer Meeting of the Institute will be held at Birmingham from May 22nd–24th, 1939, under the Presidency of Professor A. W. Nash, M.Sc., M.I.Mech.E. The objects of the meeting are to review and interpret recent work on fuels and lubricants for use in internal combustion engines.

The programme of the meeting, together with details regarding Ladies' Visits, Registration, etc., are given in the circular sent out separately to members.

A summary of the programme is given below :

Monday, May 22nd.

Evening.	Informal Reception by the President at the Grand Hotel, Birmingham.

Tuesday, May 23rd.

Morning.	Technical Session.—Knock-Rating.
Afternoon.	Technical Session.—Lubrication.
Evening.	Reception in the Grand Hall, The University, Edgbaston.

Wednesday, May 24th.

Morning.	Technical Session.—Fuels for Compression-Ignition Engines; Lubrication.
Afternoon.	Visits to Austin Motor Company and Morris Commercial Cars Ltd.
Evening.	Dinner and Dance at the Grand Hotel.

TRANSFERS TO NEW CLASSES OF MEMBERSHIP.

The Council has approved the following transfers from Member to Fellow. The omission of any Member's name from this List does not imply that his application has been disallowed. Several hundreds of applications have been received and are awaiting consideration. A further list will be published in the May *Journal*, which will also contain transfers approved from Associate Members and Associates.

Members who wish to transfer to one of the new classes of membership are requested to submit their applications as early as possible on the forms provided for the purpose at the back of the leaflet convening the Special General Meeting held on 10th January, 1939.

Transfers from Member to Fellow.

Adam, W. G.
Anfilogoff, N. A.
Anfilogoff, N. L.
Attwooll, A. W.
Aylwin, W. E.

Baldwin, R. F. A.
Ball, H. S.
Banks, B. G.
Banks, F. R.
Banks, M. A. L.
Banta, C.
Barber, C. T.
Barringer, K. A.
Barton, C. H.
Barton, D. C.
Bassett, H. N.
Baylis, A. N.
Beale, E. S. L.
Bentz, A.
Blackler, M. B.
Blank, M. De
Bleeck, R. L.
Boaden, E.
Bolton, R. P.
Bowen, A. R.
Bowrey, S. E.
Brame, J. S. S.
Brey, J. H. C. de
Broom, W. E. J.
Broome, D. C.
Brown, C. B.
Buck, E. C.
Burgess, S. G.

Cadman, W. H.
Cameron, I.
Carpenter, J. A.
Carter, Ashley.
Catherall, A. P.
Chalk, L. J.
Chambers, A. E.
Chapman, A. H.
Charlton, H. E.
Chilvers, C.
Clapp, F. G.
Clark, L. V. W.
Clark, P. R.
Clayton, D.
Clement, L.
Cohn, T. H.
Connock, R. F.
Cox, A. W.
Cunningham-Craig, E. H.

Dabell, C.
Dawidson, E.
Dean, E. W.
Delbridge, T. G.
Dewhurst, T.
Dickson, C. B.
Dorrell, G. W.
Dunstan, A. E.
Dyson, G. M.

Edeleanu, I.
Eldridge, R. A.
Elias, G.
Engel, B.
English, W.
Evans, C. E.
Evans, E. A.
Evans, E. B.

Fancher, G. H.
Fay, E.
Fordham, W. H.

Gabriel, L. G.
Garlick, H. S.
Garner, F. H.
Garton, F. L.
Gibson, G. W. E.
Gilbert, C. L.
Gilbert, R.
Godet, R.
Golyer, E. de
Gooday, W. E.
Goodwin, J. A.
Gordon, K.
Goulston, W. W.
Gregory, J. L.
Grey, R. G.
Guthrie, J. T.

Hague, E. N.
Harrap, F. N.
Harris, J. L.
Hartley, A. C.
Haslam, J. E.
Heaton, W. B.
Henderson, W. H.
Henny, V.
Herbert, E. LeQ.
Hill, C. V.
Hill, J. B.
Hoffert, W. H.
Holley, A. E.
Hope, A. E.
Hope, V. V. L.
Hotham, E.
Howard, F. E.
Howe, W. H.
Hubbard, M. E.
Hughes, J.
Hunter, C. M.

Ireland, S. J.

Jackson, J. S.
Jarrett, W. T.
Jelffs, W. F.
Jennings, J. C.
Johnson, E. C.
Kay, J. B.
Kay, W.
Keep, C. E.
Kelly, C. I.
Kerr, P.
Kewley, J.
Koefoed, H. G.
Kreulen, D. J. W.
Kugler, H. G.

Launy, S.
Lavington, H. V.
Lepper, G. W.
Leslie, R. W.
Lieshout, C.

Macfadyen, W. A.
Mandelbaum, M. R.
Miller, W.
Milner, H. B.
Myddleton, W. W.

McCarthy, M. P.
McIntyre, G.
McLuckie, A. D.

Nabuco, C. E. de Araujo
Neilson, R. G.
Nixon, G. R.

Odams, R. C.
Ogston, A. R.
Owen, L.
Owen, R. M. S.

Parrish, J.
Penny, F. W.
Peutherer, W. B.
Phelps, A. W. H.
Pilat, S.
Pitkethly, R.
Potter, F. M.

Read, A. L.
Redgrove, E. R.
Richardson, A. W.
Roger, R. H.
Rosaire, E. E.
Ruthven-Murray, A. J.

Sachs, A. P.
Sager, F.
Samuel, D. L.
Sanders, J. M.
Scott, F. H.
Sell, G.
Sickle, R. K. van
Simpson, A. T. S.
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Smith, A. D.
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Vachell, E. T.
Vaschalde, A.
Vincall, G. J. C.
Wade, A.
Walter, G.
Ward, P. J.
Ward, R. J.
Werrett, L. A.
Weston, L.
Weymarn, P. von
Wigney, W. J.
Wilde, H. de
Wilford, A. T.
Wilson, R. E.
Wilson, W. J.
Wood, C. E.
Wood, C. W.
Woodrow, W. A.
Wood-Mallock, J. C.
Young, C. R.
Zavoico, B. B.

NEW MEMBERS.

The following elections were made by the Council in accordance with the By-Laws, Section IV, Para. 7, at the Council Meeting held on Friday, 17th March, 1939.

Elections are subject to confirmation in accordance with the By-Laws, Section IV, Paras. 9 and 10.

Fellows.

Allen, Samuel	Surrey.
Annan, John Greig	Edinburgh.
Braybrook, Frederick Houghton	London.
Cumming, William Murdoch	Glasgow.
Eck, Jan Carel van	London.
Fleming, Alexander	Edinburgh.
Godber, Frederick	London.
Grant, George	Pumpherston.
Grant, James	Suez.
Gray, William	Pumpherston.
Guy, William Robert	Broxburn.
Heath-Eves, Hubert Bryan	London.
Kessler, Jean Baptiste August	London.
Legh-Jones, George	London.
Macmillan, William Hutchinson	Edinburgh.
McColl, Alexander Lowe	London.
Napier, John Watson	Alloa.
Preston, Richard	Bucks.
Sellers, Richard Willcox	London.
Stewart, Daniel	Broxburn.
Trueman, Arthur Elijah	Glasgow.

Members.

Annan, John Greig, Jr.	Edinburgh.
Balloch, Alexander	Grangemouth.
Blane, Edward Richardson	Surrey.
Caldwell, John Martin	Pumpherston.
Crombie, John James	Pumpherston.
Fleming, Peter	Grangemouth.
Forbes, Christopher Ewart	Uphall.
Fox, Reginald William Lansby	London.
Hanforth, William Percival	Singapore.
Hannah, Edwin George	Essex.
Heseltine, Guy Robert Nelson	London.
Hobbs, Frederick James	Brazil.
Inglis, Andrew Goldie	Grangemouth.
McCallum, John	Uphall.
MacDowall, Robert Kennedy	Oxford.
Paul, David	Uphall.
Thomson, Robert Cunningham	Grangemouth.
Thorneycroft, Thomas Hamo	Glasgow.
Tripney, James Sharp	Winchburgh.
Wrixon, Reginald Bryan Bentley	Egypt.

Transfer to Member.

Chastelain, Alfred George de	Roumania.

Associate Members.

Fox, Denys Anthony	Abadan.
Gordon, Jackson George	Glasgow.
Green, Stanley George	London.
Helcke, Herbert Leslie	Grangemouth.
Johnston, Thomas Alexander	Edinburgh.
Meikle, John	Edinburgh.
Nisbet, Thomas	Grangemouth.
Robertson, George Gray	Bo'ness.

Transfer to Associate Members.

Stibbs, Edward George	Trinidad.
Ward, Ernest Richard	Burma.

Students.

Bogdo, Perlat	London.
Bruce, Patrick David	London.
Carder, William Aubrey	Sevenoaks.
Clarke, Geoffrey Jardine	London.
Edwards, Guy Norman Peerless	London.
Everett, Eric George	London.
Hall, Alan Elmo	U.S.A.
Hanchard, Kenneth William	Essex.
Janion, Laurence Pendell	Brighton.
Mason-Pay, Philip Anthony	Southend.
Mountford, Lawrence Almeric	Loughton.
Murphy, Brian Aloysius	Australia.
Pickard, William Thomas	London.
Sisley, Harold	Surbiton.
Steuart, Daniel	Edinburgh.
Wormald, Stanley Allen	Pinner.

CANDIDATES FOR ADMISSION.

The following have applied for admission to the Institute or transfer to another grade of membership, and in accordance with the By-Laws the proposals will not be considered until the lapse of at least one month subsequent to the issue of this *Journal*, during which any Member or Associate Member may communicate by letter to the Secretary, for the confidential information of the Council, any particulars he may possess respecting the qualifications or suitability of any candidate.

The object of this information is to assist the Council in grading candidates according to the class of membership.

The names of the candidate's proposer and seconder are given in parentheses.

Arter, Kenneth Troward, B.Sc., A.M.I.A.E., Engineer (*Esso European Laboratories*), 94, Southdown Avenue, London, W.7. (*F. H. Garner ; T. Wilford.*)

Bennett, John Alfred, Oil Sales Manager (*Silvertown Lubricants, Ltd.*), 10, Fairway, Raynes Park, London, S.W. 20. (*E. A. Evans ; E. C. Styles.*)

Bowring, Frederick Beakbane, Inspection Engineer (*Trinidad Leaseholds Ltd.*), Forest Reserve, Fyzabad, Trinidad, B.W.I. (*J. L. Harris ; G. Mardall.*)

Browne, Richard Vernon, Geologist (*Petroleum Development Ltd.*), P.O. Box 310, Nicosia, Cyprus.

Bune, John Norman, Clerk (*Anglo-American Oil Co., Ltd.*), 15, Reed Pond Walk, Gidea Park, Essex. (*A. Hamilton ; C. Chilvers.*)

Chandler, Richard, B.Sc., Process Chemist (*Bahrein Petroleum Co.*), Homelands, Strete, Dartmouth, S. Devon. (*A. W. Nash ; L. V. W. Clark.*)

Collier, Alan, Industrial Chemist (*L.T.C. Distillates, Ltd.*), "West View," Rectory Lane, Duckmanton, Chesterfield, Derbys. (*G. S. Pound ; H. G. Shatwell.*)

COOPER, Reginald Bruce, Chemist (*Shell-Mex & B.P., Ltd.*), Lensbury Club, Broom Road, Teddington, Middx. (*F. N. Harrap ; C. B. Rowntree.*)

DRISCOLL, Ernest Percy, M.Sc., A.I.C., Chemist (*Anglo-Iranian Oil Co., Ltd.*), 50, Green Moor Link, Winchmore Hill, London, N. 21. (*D. G. Smith ; R. Stansfield.*)

ELLIS, Stephen Robert Mercer, M.Sc., Chemist (*Low Temperature Distillates, Ltd.*), 14, Old Hill, Bolsover. (*G. S. Pound ; H. G. Shatwell.*)

GOODALL, Kenneth William, Chemist (*Standard Telephones & Cables, Ltd.*), 26, Claremont Square, London, N.1. (*H. Moore ; R. B. Hobson.*)

HOLBECHE, Geoffrey James, Sales Engineer (*Marine & Industrial Lubricants, Ltd.*), 25, Park Court, Hampton Wick, Kingston-on-Thames. (*G. W. D'Arcy Evans ; E. J. Dunstan.*)

NOOHI, Khalil, B.Sc., A.R.S.M., Student, c/o Imperial Iranian Legation, 50, Kensington Court, London, W. 8. (*V. C. Illing.*)

PATRICK, John Shaw, Mechanical Engineer (*Shell Central Laboratories*), 10, Lower Park, 54, Putney Hill, London, S.W. 15. (*J. S. Jackson ; J. Parrish.*)

RAMSAY, Eric William, B.Sc., Engineer (*Texas Company (S.A.), Ltd.*), c/o P.O. Box 714, Cape Town, S. Africa. (*W. E. Gooday ; R. V. Wheeler.*)

SHAND, Walter Munro, Foreman Operator (*Low Temperature Distillates Ltd.*), 87, Dukes Drive, Newbold, Chesterfield, Derbys. (*W. F. Murray ; A. D. McLuckie.*)

TRAFFORD, Edward le Marchant, Drilling Superintendent (*Trinidad Leaseholds Ltd.*), Pointe-a-Pierre, Trinidad, B.W.I. (*F. A. L. Tindall ; H. C. H. Thomas.*)

TEALE, Ronald Sowerby, Chemist (*Asiatic Petroleum Co., Ltd.*), "Farnley," St. Michael's Green, Beaconsfield, Bucks. (*J. Kewley ; C. H. Barton.*)

WATSON, Karl, Chemist (*Low Temperature Carbonisation Ltd.*), "Twenty One," Houghton Road, Bolsover, Chesterfield. (*R. C. Odams ; G. S. Pound.*)

WILSON, Edward Richard, Assistant Manager (*Anglo-American Oil Co., Ltd.*), 6, Canterbury Drive, Sedgley Park, Prestwick, Manchester. (*J. E. Haslam ; L. R. Roberts.*)

STUDENTS' MEDAL AND PRIZE.

The Council has decided that the Students' Medal and Prize in 1939 will be awarded for a thesis on a set subject, and not for theses on subjects chosen by the candidates themselves.

A short list of alternative subjects on which theses are invited will be issued by the Council to all Students of the Institute after 30th June, 1939.

ARTHUR W. EASTLAKE,
Honorary Secretary.

PERSONAL NOTES.

Mr. W. J. BAKER has returned to Iran.

Mr. S. C. R. COOPER is home from Roumania.

Dr. D. A. HOWES is home from Iran.

Mr. M. E. KELLY is home from Iran.

Mr. M. A. RHYS PRICE has left Trinidad and is now in England.

Dr. M. L. STEINSCHNEIDER is now in England.

Correspondence or *Journals* forwarded to the following members have been returned, and the Secretary would be pleased to receive any information regarding their present address: E. C. BROWN, K. BURTON, M. CAPPER, O. C. ELVINS, V. C. S. GEORGESCU, J. J. L. HAMILTON, J. R. HORTH, A. D. JONES, J. LANDER, H. R. LOVELY, I. LUSTY, F. MACKLEY, A. MACLEAN, G. P. MELVILLE, C. A. MOON, S. NICOL, S. PAPP, R. G. REID, N. D. ROTHON, R. W. SMITH, H. G. SPEARPOINT, and P. F. THURLOW.

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BY

LS

City, N.Y.

VOL. 25. No. 186. APRIL 1939.

THE DEVELOPMENT OF FUELS FOR AUTOMOBILE ENGINES.*

BY THE INSTITUTE OF PETROLEUM KNOCK-RATING COMMITTEE.

SUMMARY.

An outline is given of the changes which have taken place in the characteristics of petrol during the last twenty to thirty years, and the requirements for good performance in modern cars are described. It is pointed out that further improvements in fuels could be made if certain alterations were effected in engine design.

The anti-knock quality of petrols has been steadily rising, and the compression ratios of car engines have also risen, largely due to the improvement in the petrols, but also because of design improvements. The cost of further anti-knock improvements in petrol, and the advantage to be gained by increases of compression ratios in engines for the average motor car, both appear to be reaching the point where they become uneconomic.

Fuels of different chemical types have different anti-knock values, and a knowledge of this has largely controlled developments in fuel refining, although the highest anti-knock fuels now available are too expensive to be regarded as potential motor fuels.

The accepted method of making laboratory tests for anti-knock value on the C.F.R. engine is described, an account is given of the procedure for conducting knock tests on the road, and the difficulties of correlating road with laboratory behaviour are discussed.

Information obtained by this Committee from road tests, in particular in relation to the effect of ignition timing, is summarized, and the hope is expressed that a more effective exchange of knowledge of the research work on engines and fuels that has been and is being conducted by various organizations will promote closer co-operation between the automobile engineer and the petroleum technologist.

IN the comparatively short space of twenty years petrol as sold to the motorist has changed almost out of recognition. It is not possible to-day to buy petrol similar to that sold in 1919, but if the motorist could do so and were to fill his tank with that fuel he would be unpleasantly astonished at the performance of his engine. It would not be possible to open the throttle without violent knocking, and in addition to the unpleasant noise, rapid overheating would result, together with destruction of the sparking-plugs and probably with pre-ignition so violent as to damage the engine. In addition the volatility characteristics of the fuels of those days were so variable that carburation difficulties would be likely to give rise to troubles only one degree less serious than those due to knocking.

DEVELOPMENTS IN FUEL VOLATILITY AND CARBURATION.

Volatility.

Petrol, as is well known, is a mixture of many hydrocarbons and therefore has not a constant boiling point; on laboratory distillation boiling begins freely at a temperature little above summer atmospheric temperatures, but distillation is not completed until a temperature of 150° C. to 200° C. is reached. In the carburettor and induction manifold, however, the light fractions help to vaporize the heavier fractions, with the result that complete vaporization occurs at considerably lower temperatures.

* Paper to be presented for discussion at the Summer Meeting of the Institute of Petroleum to be held in Birmingham 22nd–24th May, 1939.

The distribution of the components through the boiling range exerts a pronounced influence on quick get-away and general acceleration. The boiling range of the fuel must be adjusted, therefore, to ensure that sufficient easily vaporized " light ends " from the excess fuel obtained by the use of the choke or " starter carburettor " device now fitted to many carburettors, are present to form a combustible mixture in the cylinder under the coldest weather conditions.

Carburation.

In the earliest days of motoring the jet type carburettor was designed without any automatic device for maintaining even a roughly constant mixture strength with changes of engine demand. The principles underlying " compensation " were not even understood. The results were so hopeless that for several years surface carburettors were preferred, and some of the most successful early engines had carburettors of this type. The surface carburettor worked well on a fuel of narrow boiling range and high volatility, but most indifferently on the " heavier " petrols. So important was it to use a " light " spirit that motorists used to carry hydrometers in their pockets, and when fuel was bought at the road-side, they would test the contents of each can to see that the specific gravity did not exceed 0·68. Detonation occurred on hills, but this was attributed to overheating, and no one thought to examine the influence of fuel characteristics on the already known phenomenon of " knocking." It is true that before the world war it was recognized that benzole was less prone to cause engine knock than petroleum spirit and, also, contained more heat units per gallon on account of its higher specific gravity, but the carburettors of the time were not designed to cope with benzole and starting from cold on this fuel was a very uncertain enterprise.

As soon as carburation began to receive serious consideration it was realized that to ensure easy starting, good acceleration, reasonably uniform distribution and freedom from vapour-lock troubles it is essential that the physical characteristics of the fuel must be carefully controlled if the fuel system as a whole is to function efficiently.

For starting purposes the carburettor delivers wet air-fuel mixture which must contain considerably more fuel than is required for normal running, due to the fact that a large proportion of the fuel is deposited on the cold walls of the manifold. The extent to which the fuel is broken up into spray when it leaves the carburettor jets is also, of course, very important, as the proportion of the total fuel vaporized bears a direct relationship to the surface area of the fuel droplets. Excessive choking leads to serious dilution of the lubricating oils and often causes flooding of the whole system, and then gives an over-rich mixture rendering starting impossible. For this reason the thermostatically controlled " starter carburettor " device which gives a controlled mixture, or the choke automatically adjusted by manifold temperatures, are much to be preferred to the manually controlled chokes.

During the acceleration period it is necessary that the carburettor delivers a mixture to the engine which will generate maximum power. This mixture should be approximately of 12 : 1 air-fuel ratio by weight, which is definitely richer than that suitable for maximum economy. The sudden

opening of the throttle will cause the pressure in the manifold to change from a partial vacuum to approximately atmospheric pressure, and under these conditions some of the less volatile constituents of the fuel are deposited as liquid on the manifold walls.

The higher the volatility of the fuel, therefore, the more readily will the richer mixture be obtained and the less time will be taken for the engine to respond.

It is customary to incorporate an auxiliary device such as an accelerator pump to give the necessary richness when required, and the performance of an engine during acceleration, therefore, depends as much on the behaviour of the carburettor as on the fuel.

Most carburettors are set to operate on fuel of average volatility, and in practice it is found that small increases in volatility tend to give smoother acceleration, a falling off in performance only occurring if the proportion of light fractions in the fuel is exceptionally high.

Distribution.

The problem of supplying a uniform mixture to the various cylinders of an engine running on liquid fuel is one of the most difficult confronting the engine designer. Except at very light loads and when the engine is hot it is very doubtful if the mixture of fuel and air ever reaches the combustion chamber in a homogeneous form. The fuel droplets, air and vapour travel through the induction pipe at the same speed, and the greater inertia of the former causes them to be thrown against the walls of the induction pipe wherever a bend in the manifold causes a change of direction. If more than two cylinders are being fed from one carburettor, symmetry and equal lengths of passage are impossible and the deposition of the fuel in the manifold causes mixtures of unequal strengths to be supplied to each cylinder. A few years ago it was common practice to cast the induction pipe in one with the cylinder block with the object of supplying heat from the water jacket. This procedure was, however, of little value, as the heating effect was not nearly sufficient to vaporize more than a small fraction of the fuel. The present practice of heating the manifold from the exhaust pipe and thus forming a " hot spot " where the mixture enters the induction pipe is much more effective, and designers are now paying great attention to induction-pipe design in an endeavour to minimize distribution troubles. It has been shown that unequal distribution may also be caused by faulty location of the fuel jet in relation to the venturi, small changes of position affecting the amount of fuel delivered to various cylinders. To obtain reasonable uniformity in the behaviour of production carburettors the use of finer tolerances in manufacture is being shown to be necessary. To ensure that an engine shall run smoothly and not suffer damage from the effects of weak mixture to individual cylinders it is necessary to supply an overall mixture on the rich side, and for this reason it is not possible to obtain such high efficiencies with the multi-cylinder engine as with the single-cylinder unit unless the complication of duplicating carburettors is resorted to. Unequal distribution is also one of the main causes of varying degree of knock often experienced in separate cylinders, and improvement in the uniformity of mixture delivered to each cylinder would improve the anti-knock

performance of a given fuel. In a conventional automobile engine the extra fuel which has to be supplied to overcome troubles from bad distribution may be as high as 10 per cent. of the fuel consumption, and thus improvements in this direction are well worth while.

Vapour Lock.

When a modern petrol is distilled and the distillate collected in separate fractions, an examination of those fractions shows that the most volatile portions usually contain the most powerful anti-knock materials.

Many natural crude oils, as well as cracked products, contain more of these volatile fractions than can be incorporated in the finished motor spirit, because if the whole of the portion were included the fuel would be liable to premature boiling in the fuel-feed lines, pump and carburettor, thus giving rise to vapour lock and consequent irregular running, especially in hot weather under strenuous driving conditions. Under present conditions, therefore, enormous quantities of the " cream " of petroleum has perforce to be wasted.

Although vapour-lock troubles are perhaps not common in this country they are, of course, very important to the car manufacturer exporting to warmer climates. The minimizing of the tendency towards failure of fuel supply due to vapour lock is a problem affecting the car designer as much as the fuel refiner, and more attention to the problem by the former could readily result in the supply of fuels of greater volatility giving easier starting, improved distribution and better anti-knock value. Even though no actual engine failure is experienced it has been shown that appreciable fuel losses occur considerably before the limit of vapour-handling capacity of the fuel system is reached, and such losses result in a reduction of the anti-knock value of the fuel reaching the engine. Improvements in the design of fuel pumps and carburettors as regards the volume of vapour they can handle has, during the last year or two, greatly reduced engine failure from vapour lock, but it is suggested that much more might be done to lessen the cause of the trouble by consideration of the layout of the fuel system as a whole, including cooler positions for or lagging of fuel lines and protection of the carburettor and fuel pump from heat radiated from the manifold and exhaust pipe. Such improvements would also help in reducing fuel consumption by minimizing loss of the lighter fractions at the carburettor. These considerations apply equally or even more particularly to commercial vehicles and buses, where the under-bonnet temperatures are greater than those existing in passenger cars owing to the relatively greater space occupied by the engine.

Developments in Engine Design and in Anti-knock Quality of Fuels.

Although the petrol of to-day is vastly superior in a considerable number of different ways to the petrol of even a few years ago, by far the most fundamentally important change has been the increase in its resistance to knocking, for it is this factor which controls the compression ratio of the engine, and consequently the fuel efficiency and power output of an engine of given dimensions.

The graph at the top of Fig. 1 illustrates the improvement in anti-knock

quality that has been achieved since 1920. The graph shows the step-by-step increases of octane number of No. 1 grade petrol, which amounts to

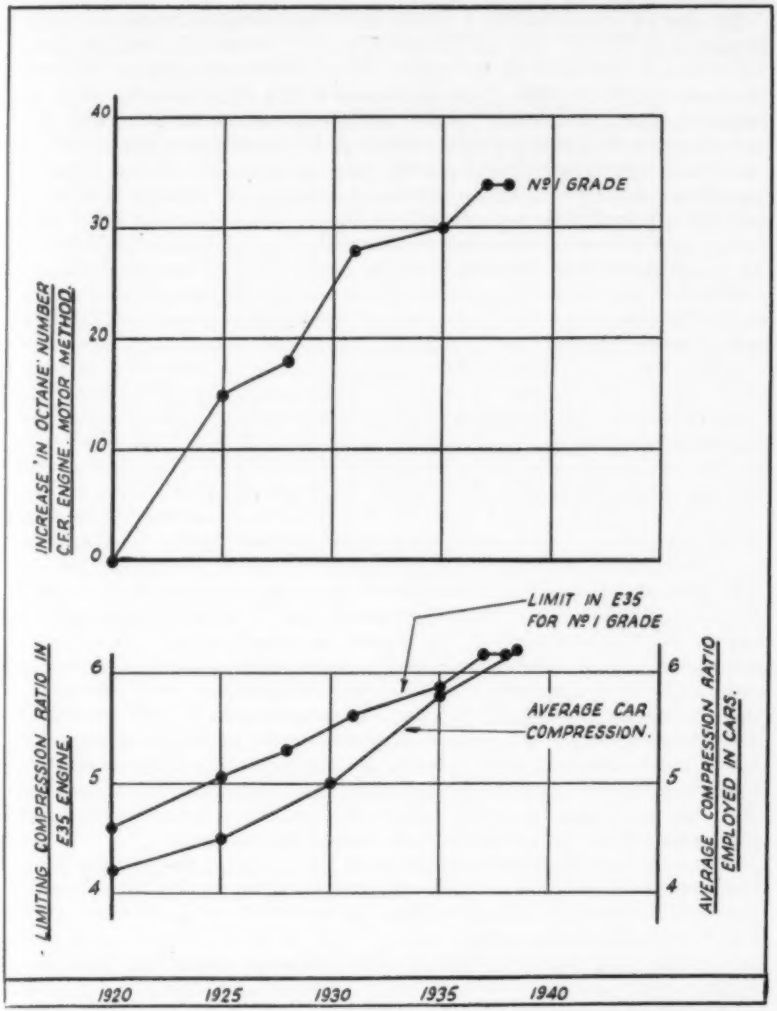


FIG. 1.

IMPROVEMENT IN ANTI-KNOCK QUALITY OF FIRST GRADE MOTOR SPIRITS, ALSO COMPRESSION RATIO USED IN BRITISH CARS BETWEEN 1920–1938 (AVERAGE VALUES).

34 octane numbers since that date. The upper one of the two lower graphs in the same figure shows the limiting compression ratio that could be used in a certain engine when running on the fuels to which the top graph refers.

It will be seen that a fuel improvement of 34 octane numbers made possible an increase of compression ratio from 4·6 to 6·15, a difference of 1·55 ratios in the particular engine referred to.

The lowest graph in Fig. 1 shows that the average compression ratio employed in British cars has increased by more than this, namely, from 4·2 to 6·2, a difference of 2·0 ratios. The diminishing distance between the lower pairs of graphs gives a measure of the improvements made in engine designs, particularly in the matter of combustion chambers and the positions of sparking-plugs. Although in recent years the improved anti-knock properties of motor fuels have been mainly instrumental in permitting the use of higher compression ratios, and although it may be possible still further to improve fuels in this respect, it does not follow that power outputs can be increased economically by such means indefinitely. As compression ratio increases the resulting increased compression and combustion pressures exert greater stresses on the component parts of the engine, and the more rapid pressure rises per degree of crankshaft rotation must result eventually in rough running from excessive shock, and consequent vibration, although this roughness can, it is true, be controlled to some extent by proper attention to mechanical and combustion-chamber design.

While increase of compression ratio in conjunction with a fuel of sufficiently high anti-knock value makes possible an increase of power and efficiency, yet the advantage obtained by successive increments of compression ratio steadily diminishes; thus the increase in power obtained by raising the compression ratio from 4 : 1 to 5 : 1 is 16½ per cent. as against 3½ per cent. from 7 : 1 to 8 : 1. The maximum pressures in the cylinder, on the other hand, rise nearly uniformly with increase of compression ratio, so that the difficulties of keeping the engine free from rough running and of keeping material costs down are increasing steadily for a rapidly falling rate of improvement in performance. As regards the fuels, it is true that a smaller increase of octane number is needed to meet an increase of compression ratio in the 7 to 8 range than in the 4 to 5 range, but the cost of increasing the anti-knock value soon becomes disproportionate to the maximum possible gain, and it seems that a general trend to higher compression ratios must necessarily be followed by an increase of fuel cost quite incommensurate with the resulting small improvement in car performance. The curves shown in Fig. 2 show the general relationship between compression ratio, power output and maximum pressures.

As may be seen from the lower graph in Fig. 1, during the past ten years the average compression ratios of cars on the British market have steadily increased by over one ratio, the average figure for 1938 being approximately 6·2 : 1, excluding the so-called " sports " type of car. With this latter type of car the rise in compression ratio over the same period has been of a similar order, but has remained fairly constant at about 6·8 : 1 for the past two or three years, and has been limited to a great extent by the anti-knock properties of available fuels and practical considerations in engine design which limit the increase in compression ratio if engine roughness and other troubles are to be avoided. During the past year or two there have in fact been instances where manufacturers have found it necessary to lower compression ratios on some models due to troubles experienced in this respect. Since 1928 the average maximum brake-

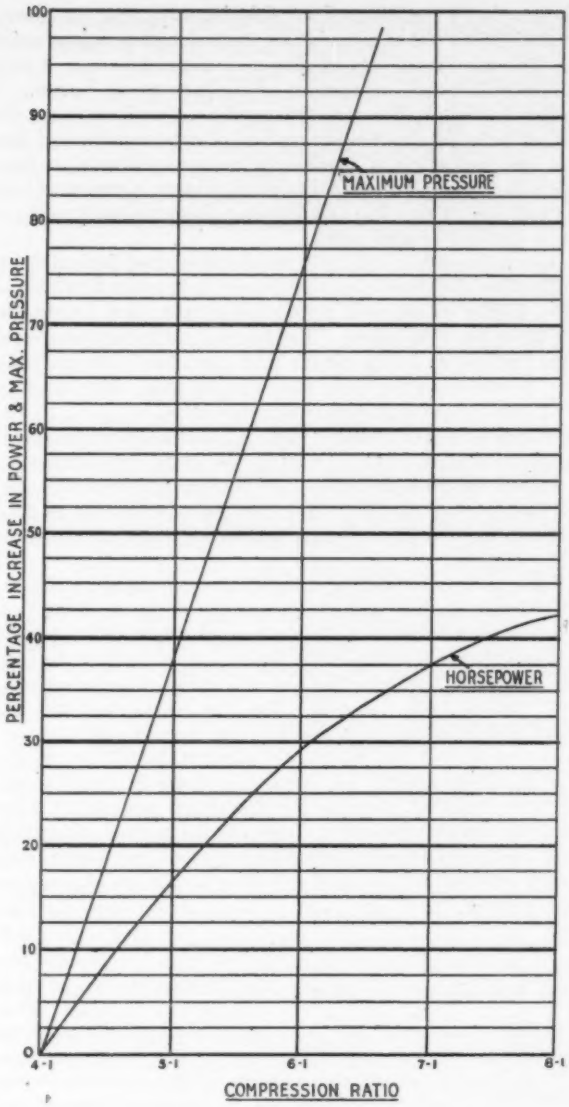


FIG. 2.

horse-power of automobile engines has almost doubled, the present average figure for maximum brake-horse-power per cubic inch of engine displacement being about 0·45.

Many factors have contributed to this improvement in power. The increase in anti-knock value of fuels has enabled higher compression ratios to be used. The increase in compression ratio alone, however, is responsible for only a relatively small proportion of the increase in power. A study of flame control has resulted in much more efficient performance. Research in this field has brought about closer control of conservation and dissipation of heat and the generation of maximum pressures relative to time in the cycle of operations in a manner best suited to the attainment of high power output, smoothness of running and freedom from undue stresses resulting from pressure shocks to engine parts.

Improvements in mechanical design too numerous to deal with separately and the utilization of improved materials of construction have all combined to permit of higher piston and rotational speeds, and bearing loads far in excess of those possible before. The average modern car engine develops its maximum power at about 4000 r.p.m., and the corresponding piston speeds may be considerably over 2500 ft. per min., whereas a few years ago 1250 to 1500 ft. per min. were more normal.

Another factor is that of cylinder size. Cylinders have tended to become smaller, and for similar engines, having the same bore-stroke ratio, and for equal stresses and bearing loads, the maximum power will vary as the $\frac{2}{3}$ power of the cylinder volume. For example, a reduction of 30 per cent. in the volume of the cylinder will increase the power per unit of volume by as much as 12 per cent.

The position as regards engine design, however, is not unlike that now existing in relation to the anti-knock quality of fuels, namely, that any further improvement is bound to become increasingly difficult though there is the difference that in the case of the fuel it is bound also to be increasingly expensive. However, scope for considerable improvement of the "average" design still remains. This is evidenced by the better performance, with freedom from knock, given by some cars than by others. The improvements will, no doubt, be effected partly by refinements in combustion-chamber design, but probably there is more scope still in providing an accurately controlled fuel mixture strength under varying load conditions and by ensuring a more definite control of ignition so that the timing is optimum at each instant for each and every speed and throttle position, and particularly for each cylinder, as the timing may vary from cylinder to cylinder.

Methods for Meeting Demand for Higher Anti-knock Fuels.

The fact that some fuels were more prone than others to "knock" was first recognized in pre-war days and became more widely known with the advent of war-time aviation, and as soon as the value of increased anti-knock quality of petrols was appreciated the question of supplies of knock-resisting fuel became important.

There were at that time certain empirical fragments of knowledge, such that some petrols, particularly those of relatively high specific gravity for a given boiling range, were less prone to knock than others and that benzole and toluole were knock suppressors, but it was not until the end of the war

that systematic research on the correlation of the chemical nature of fuels with their knocking characteristics was started.

It was found that, in general, the aromatic hydrocarbons (benzole, toluole, etc.) which exist in coal-tar, and to small and varying degrees in most petroleums, are very knock-resistant, that the naphthene series of hydrocarbons (C_nH_{2n}) rank next, followed by the olefines (C_nH_{2n}), while the paraffin series of hydrocarbons (C_nH_{2n+2}) varied greatly, some being very good but many very bad. Outside the hydrocarbon range alcohol was found to possess good anti-knock qualities, exceeding even those of benzole or toluole.

Parallel with and aided by this preliminary knowledge the search for improved fuels from the anti-knock standpoint continued. At first the only method of meeting the demand was to examine petrols distilled from a series of crudes and to select those which permitted the highest compression ratio to be used in a given design of engine without the incidence of knock. It was obvious, however, that means must be found for augmenting these rather limited supplies for the demands of the very rapidly increasing number of engines in use.

Benzole was a valuable material for use as a blending agent to improve anti-knock qualities, but the quantities available were too small to meet all requirements. Alcohol was suitable in some respects, but had disadvantages which at that time had not been overcome in a commercially satisfactory manner. Petrols containing relatively large percentages of aromatic compounds (the class of hydrocarbons of which benzole is representative) and also those consisting predominantly of naphthenes were found to be desirable, while paraffinic fuels tended to knock badly.

Shortage of the light fractions of crude oil for use in petrol engines was being felt apart altogether from the question of anti-knock properties, and rapid developments were taking place in refineries practice in the installation of a variety of " cracking " processes.

These processes, developed in the early stages to augment output, aimed at converting heavy oil into a product from which further petrol could be distilled, the conversion depending on controlled application of pressure and temperature to the raw material.

Not only was cracking successful as a means of increasing supplies, but it was found that, in practically every instance, the petrol formed by cracking had a higher anti-knock value than the motor fuel obtained by a straight distillation from the same crude, so that " cracked petrol," formerly regarded as inferior to " straight run petrol," now came to be preferred.

Concurrently with this development a search inseparably linked with the names of Midgley and Boyd was proceeding for means for raising anti-knock value by using certain chemicals added in relatively small concentrations to the petrol. Many thousands of these were tested and a few were found to possess more or less potency as " anti-knock dopes," though still fewer ever reached the market.

Aniline and toluidine were tried with limited success for special purposes, but had serious disadvantages, as well as being too expensive to be economically justifiable. Iron carbonyl was also partially successful, but could be used only in small concentrations and was not free from difficulties.

The only commercially satisfactory concentrated anti-knock compound

so far discovered is lead tetra-ethyl, and this now is used in many countries for a considerable proportion of the motor fuels marketed.

A recent development, at present confined almost entirely to aviation fuels, is the production in the oil refineries of synthetic hydrocarbons such as *iso*-octane or other synthetic fuels such as *di*-isopropyl ether which are characterized by extremely high anti-knock qualities. They cannot, however, be regarded as potential motor-car fuels on account of cost. There are, however, other synthetic hydrocarbons of lower, but still quite good anti-knock rating which are sufficiently plentiful to be used as blend stock for raising the general level of anti-knock quality in ordinary motor fuel.

While the records of the past decade show a year-by-year increase in the general anti-knock quality of motor fuel, brought about by more intensive cracking and by the use of benzole, alcohol, lead tetra-ethyl or synthetic hydrocarbons, such an increase is slowing down and cannot be continued indefinitely. Each augmentation of octane number becomes progressively more costly, until apart from special cases (such as racing or special aircraft fuels) it must inevitably become uneconomic.

It is dangerous ever to predict that further improvement is impossible, but, as far as can be seen to-day, the cost of any considerable increase of anti-knock value above present British standards (the highest in the world) is unlikely to be worth while.

Methods of Testing and Rating the Anti-knock Quality of Fuels.

Although attempts have been made from time to time to deduce anti-knock quality from various physical properties such as specific gravity, calorific value and aniline point, it was accepted at an early stage that the only method of laboratory test at all useful must be some form of test on a standardized engine which will give a numerical expression of "anti-knock-rating" on a universally accepted scale.

Early Methods.

Before the war Hopkinson had proved the existence of detonation in an engine as a phenomenon quite distinct from pre-ignition. The earliest tests in which different fuels were compared for anti-knock quality and given values in this respect were made in 1919 by Ricardo in his "E 35" variable compression engine. Each fuel was matched in knocking tendency with a blend consisting of measured proportions of toluene and a special aromatic-free petrol. Since toluene had a very high anti-knock value and the petrol had a low one, almost all the fuels examined could be evaluated in terms of the toluene percentage in the blend with which each was matched.

Later it was found necessary to evaluate certain fuels having lower anti-knock values than the aromatic-free petrol itself, and the continued use of the toluene scale for these fuels would therefore have involved the use of negative toluene numbers. Largely for this reason and also because of the difficulty at that time of maintaining supplies of a standard low anti-knock fuel, it was decided to abandon the matching method and to evaluate the fuels in terms of the limiting compression ratio observed in the E 35 engine under certain specified conditions. This limiting

compression was referred to as the H.U.C.R., or highest useful compression ratio. The conditions of test involved maintaining constant the engine speed, the temperature of the air intake, the cooling water temperature and the ignition timing for each compression. The last was adjusted according to the compression ratio in accordance with a predetermined curve of optimum timing, but was not varied for different fuels. The fuel-air ratio was adjusted for each fuel, so that the maximum knock-mixture strength was maintained throughout each test. The test of each fuel then consisted in raising the compression until the degree of detonation caused audible knock and no further increase of power as shown by a sensitive dynamometer. The compression ratio giving maximum power under these carefully controlled conditions was then termed the H.U.C.R. of the fuel.

A report on the early research work in England was published in 1921 and important commercial results followed almost immediately. Petroleum distillates from several different oilfields could now be blended to produce motor spirits to a predetermined standard of anti-knock value which hereupon began to take its place as a clause in specifications.

During this period research was proceeding in other countries, particularly in the United States where a Delco engine was being used. Electro-mechanical means were provided for indicating the degree of detonation, the device developed being known as the " bouncing-pin " indicator. When the engine was operated at a comparatively low speed, the bouncing pin worked well, and though a variety of other methods of indicating the degree of knock, such as audibility, audimeters, maximum power record and temperature records, were tried a development of the bouncing-pin apparatus is in use to-day in the C.F.R. engine which forms the basis of the present international standard method for testing the anti-knock quality of petrol.

The Modern Method of Knock-rating.

In 1928, under the auspices of the American Society of Automotive Engineers, the Co-operative Fuel Research (C.F.R.) Committee in the U.S.A. set up a sub-committee to develop a standard method of knock-rating, and it is due to the long, laborious and painstaking researches of this committee and the industrial resources supporting it that to-day, throughout the world and irrespective of any other method which may be used to suit local circumstances, the C.F.R. knock-testing engine with the " octane number " system of rating is used as the standard method for assessing this quality.

The scale chosen by the C.F.R. Committee, on the recommendation of Graham Edgar, for rating a fuel was based on the discovery that two pure and universally reproducible hydrocarbons which had practically the same boiling points and densities possessed extremely different resistances to knock. The fuel of high resistance was *iso*-octane (2 : 2 : 4-tri-methyl pentane), and that having an extremely low resistance was *n*-heptane. The anti-knock rating of a petrol was given by matching its knocking properties against those of prepared mixtures of these two fuels, and its value was expressed in " octane number " which was the percentage by volume of *iso*-octane in the matching mixture. By definition, therefore, *iso*-octane has an octane number of 100 and *n*-heptane an octane number of 0.

Owing to the high cost of these pure substances and for other reasons it is convenient to use, instead of *iso*-octane and *n*-heptane, a series of special petrols which cover the whole range of octane ratings likely to be required. These special petrols are termed secondary reference fuels, and they represent sub-standards of which the octane numbers have been very accurately determined.

The standard C.F.R. engine is a single-cylinder unit arranged for continuous variation of the compression ratio between the limits of 4 : 1 and 10 : 1. The cylinder has a screw thread turned outside the lower end of the bore engaging with a surrounding nut on which a worm wheel is formed. The nut is held from up-and-down movement, but is free to rotate on the operation of a worm from a suitable handle. This rotation raises or lowers the cylinder in relation to the engine crankcase, permitting the ratio to be adjusted while the engine is running. The design is of the overhead valve type with the cylinder and the head in one casting, and the inlet valve is masked to give sufficient turbulence for steady knock. The engine has a bore of 3·25 in. and stroke of 4·50 in. and is run at a constant speed of 900 r.p.m. $\pm$ 3 r.p.m.

Ignition is controlled by a link mechanism actuated from the cylinder, so that the setting is retarded as the compression ratio is increased, and stability of timing and also the actual ignition point can be observed by means of a neon tube indicator working against a protractor scale.

The cooling is evaporative with distilled water, so that the jacket temperature is maintained at 212° F., and the circulation is very rapid.

Mixture temperature is adjustable by an electrically heated system in the inlet pipe between the carburettor and the cylinder, and is maintained at 300° $\pm$ 2° F.

Even the exhaust system is sufficiently standardized to avoid the disturbing effects of non-standard back pressure.

The carburettor is of the multiple bowl type so arranged that the air-fuel ratio can be easily adjusted, and the engine run on any of three or four different fuels merely by operating a change-over cock.

Knock is measured by means of a bouncing pin in conjunction with a knock-meter. The bouncing pin is now a well-known instrument consisting of a light steel rod held by very light spring pressure against a thin steel diaphragm which is mounted in a suitable hole in the combustion chamber. Knock effects set the diaphragm into vibration and the onset of the vibration gives the pin a sharp kick, and lifts it with the pressure spring against a second spring. A pair of contacts is arranged between the springs so that electrical contact is made when knock occurs, and this contact is maintained for a time interval depending on the knock intensity. Current flows through the contacts when they are together and through a small resistance or heater coil associated with the knock-meter. This coil is thus raised to a temperature which varies with knock intensity. A series of thermo-couples mounted inside the heater coil is used to indicate the coil temperature on a millivoltmeter scale graduated from 0 to 100, and the readings on this scale thus serve to show the operator how the knock intensity alters with change of fuel or other changes of running conditions.

Tests are made by first checking the general adjustment of the bouncing pin and engine in a precisely defined manner and then running the engine

on the petrol sample with the compression ratio adjusted to give a knock-meter reading of approximately 50 at the air-fuel ratio for maximum knock. Blends of calibrated secondary standards of known octane numbers which knock slightly less and slightly more than the sample are then selected by trial and error, the knock-meter being used for comparison purposes. Inspection of knock-meter readings of the two standard blends and of the bracketed sample then enables a very closely repeatable knock-rating to be made, which can be expressed in octane numbers.

In the early days of knock-testing on the C.F.R. engine it was found that results from engine to engine and from one laboratory to another were by no means as reproducible as was desirable. Later, co-operative tests were arranged between a large number of laboratories, and it was found that precision of control of engine manufacture and operating conditions were essential for good results. Now there is little excuse for deviations of more than two octane numbers between ratings of a given fuel in different engines in different parts of the world, and in engines in one laboratory, where control is standardized, such deviations should not exceed one half of this.

The need for precise control of the engine is often looked on as a disadvantage, but it is in fact a very useful merit, because adjustment of almost any of the controllable conditions of test can be used to alter relative knock-ratings, and thus to govern the relation between laboratory ratings and those determined in cars by road tests.

Reduction of mixture temperature by 100° F. may, for example, completely reverse the ratings of two fuels, say, two octane numbers apart. Alteration of running speed also affects relative as well as absolute value of ratings. Ignition advance has a similar effect, and even instrumentation with an apparatus other than the bouncing pin, while quite satisfactory in several forms, has its own small effect on ratings.

In the foregoing description of the C.F.R. engine and the conditions of speed and fuel mixture temperature under which it is operated no mention has been made of the reasons why these particular conditions of test have been selected. It is obvious that if the relative ratings of various fuels as indicated by their octane numbers on the C.F.R. engine bore little resemblance to their relative ratings in a motor car on the road, octane values would be useless. Consequently, a tremendous amount of experimental work has been carried out since 1932 in America and in this country in correlating the road behaviour of fuels with their behaviour in the C.F.R. engine under various operating conditions.

In the earliest days of the C.F.R. engine the defined conditions of use involved a lower speed (600 r.p.m.) and an unheated mixture. These conditions constituted the " C.F.R. Research Method of Test," but correlation by this method with road behaviour was not satisfactory and when more extensive data were available it was found necessary to modify these conditions to a higher speed and a mixture heated to 300° F. These conditions gave much better general agreement with average road results and became the current standard method known as the " C.F.R. Motor Method of Test." They are based on extensive road tests made at Uniontown, Pa., in 1932 and in 1934 and a large amount of later work both in America and England.

Two points however should here be emphasized. First, since even a

carefully designed and accurately controlled test engine is very sensitive to variations in test conditions it is not surprising that knock-ratings made under inevitably much more variable conditions during road tests in ordinary cars show wide deviations; even two cars of the same make and type rarely give complete agreement as regards either knock intensity under similar running conditions or actual fuel ratings. Consequently, the test method, however defined, can only hope to give correspondence with average road results, and must not be expected invariably to fall into line with all types of fuels and all types of cars.

Secondly, changes in engine design and conditions of operation as well as changes in the nature of fuels is inevitable, and to maintain reasonable correlation it may in time be necessary to change equivalently the conditions of the test method. For this reason it is essential in the future as in the past that the Motor Method should from time to time be re-examined in the light of the cars and the fuels coming forward and, if and when necessary, revised. At the moment, however, there appears insufficient justification for any alteration of the current method.

Repeated attempts have been made over the past few years to obtain improved correlation between C.F.R. ratings and the users' acceptance of marketed fuels, but further progress would seem to be dependent on a different appreciation of what is required from the road tests, and not on immediate alteration of the C.F.R. engine or its working conditions.

The Problem of Co-ordinating the Laboratory Ratings with the Road Ratings.

It has already been pointed out that the C.F.R. Motor Method of Test is she outcome of parallel road and laboratory experiments with a wide range of fuels and cars. The laboratory octane numbers thus arrived at represent nothing more than a general average rating and take no cognisance of exceptional cases either as regards car or fuel.

It is sometimes necessary to carry out road tests on an individual fuel to find out if its road rating departs from that of the "average fuel."

Furthermore, any one car may rate a number of fuels in a different order from the "average" car. Not only may car engines of different makes place a number of fuels in different orders of merit, but there are sometimes considerable variations between the fuel ratings given by cars of the same make and type. The reason for this is that there are so many variables which may provide an almost infinite number of combinations of running conditions, and each type of fuel will respond a little differently to each of these combinations of conditions.

The features affecting the behaviour of an engine on a given fuel may be divided into three groups.

(1) Those dependent on the design of the engine, such as :—

compression ratio,
shape of combustion chamber,
valve porting and timing,
temperatures of surfaces exposed to the combustion,
shape of manifold for best distribution,

design of carburettor,
strength of spark,
back pressure of exhaust system,

and many other smaller details.

(2) Those dependent on adjustments of the engine, such as :—

carburettor settings,
ignition timing,
valve tappet clearances,
good mechanical condition of the engine and cooling system.

(3) Those dependent on climatic conditions, such as :—

humidity,
altitude,
atmospheric temperature, etc.

Up to the present time the suppliers of motor spirit have been faced with the very difficult problem of producing one or two grades of fuel which will suit cars of which the requirements approximate to the average, and at the same time will not cause serious detonation in the remaining types which may probably need a fuel of higher anti-knock rating. The number of car types in this more exacting category is only about 5 per cent. of the whole.

The solution to the problem is not easy. Owing to the enormously increased consumption of motor spirits and the modern demand for high anti-knock petrol, the days are long past when the oil industry just evaporated a crude petroleum from any source and distilled the lighter fractions for motor spirit. The problem is now vastly more complex, since it involves the special treatment of distillates from many sources and finally the blending of the resulting products to give perhaps several grades each of uniform quality. It would be a great advantage if the fuel producer could look ahead in designing his fuel, yet he does not know what the requirements will be until next year's car models are made and tried out on the road. In order to overcome this disadvantage as far as possible each year the oil companies purchase a large number of cars of the latest type and conduct extensive road tests which will tell them what fuel they were expected to have been preparing the year before. It should be a comparatively easy matter for co-operative work between engine designers and fuel suppliers to be done in this country which would result in fewer cases of engines being unsuitable for the fuels available, or *vice versa*, and which would, of course, be of considerable benefit to both the motor manufacturer and the fuel supplier.

Road Tests.

The following paragraphs contain a short description of the road tests which are at present carried out by the oil companies either jointly, under the auspices of the Institute of Petroleum, or individually.

Cars, after running at least 5000 miles since being decarbonized, are carefully tuned to the makers' recommended settings, such tuning covering the carburettor, valve and ignition settings, together with a check on the

automatic advance curve of the ignition distributor. This latter check is admittedly one which can only be done with special equipment, but, unless it is carried out, it introduces an unknown variable which may well have disastrous effects on the usefulness of the tests.

Since volatility, vapour pressure and chemical properties can easily be controlled in the laboratory, the most important test on the road is to find out the anti-knock requirements of each car and of the " average car." Conversely, the anti-knock values must be determined for a number of different fuels in a given car, and since all knocking tests must necessarily be of a comparative nature, the degree of knock obtained on a fuel under test must be recorded as better or worse than that obtained on fuels of accepted anti-knock value; such known fuels may be either blends of high and low octane sub-reference fuels as used in the C.F.R. laboratory tests, or preferably commercial motor spirits of known value which are more likely to have the same volatility as the fuel being tested.

Road Test Technique.

A method of test has been devised and standardized by the Institute of Petroleum in conjunction with the American Co-operative Fuel Research (C.F.R.) Committee, which is one of a group of committees consisting of members appointed jointly by the oil and automobile industries; together with representatives of certain Government Departments.

A flexible pipe is taken from the suction side of the petrol pump to the inside of the car so that the free end may be connected with or dipped into a can of any one of several test fuels.

After thoroughly warming the engine and transmission, the car is accelerated at full throttle from 10 m.p.h. in top gear up a slight gradient until the knock is finally extinguished, the knock intensity as determined by ear being recorded on a log sheet at steps of 5 m.p.h. The knock is mentally divided into a suitable number of intensities between maximum and zero. When the tests have been repeated several times to ensure good average results, curves of knock intensity are plotted against speed, and the anti-knock value of the various fuels can be assessed by the relative position of the curves. (See Fig. 3.)

As each fuel has to be tested several times on each car, it can be seen that tests such as have recently been carried out by the Institute of Petroleum involving thirty cars and nine fuels, together with sufficient blends of reference fuel to get one which is better and one worse than each of the test fuels, necessitate a very considerable quantity of work and expense.

As a result of the British road tests carried out in conjunction with similar but much more extensive tests in America in 1937, it was decided that although the present C.F.R. " Motor Method " of testing for anti-knock value is not perfect, no more acceptable method of laboratory test could be devised at that time.

In addition to the anti-knock rating, tests have to be devised to determine how individual cars can handle fuels of various volatilities and vapour pressures.

All of these tests involve research into carburation, distribution, ignition timing and, in fact, all the variables referred to earlier in this section.

Carburation Adjustment.

For example, exhaust-gas analyses are made first to get an idea of the general characteristics of the carburettor; if the ratio is obviously much

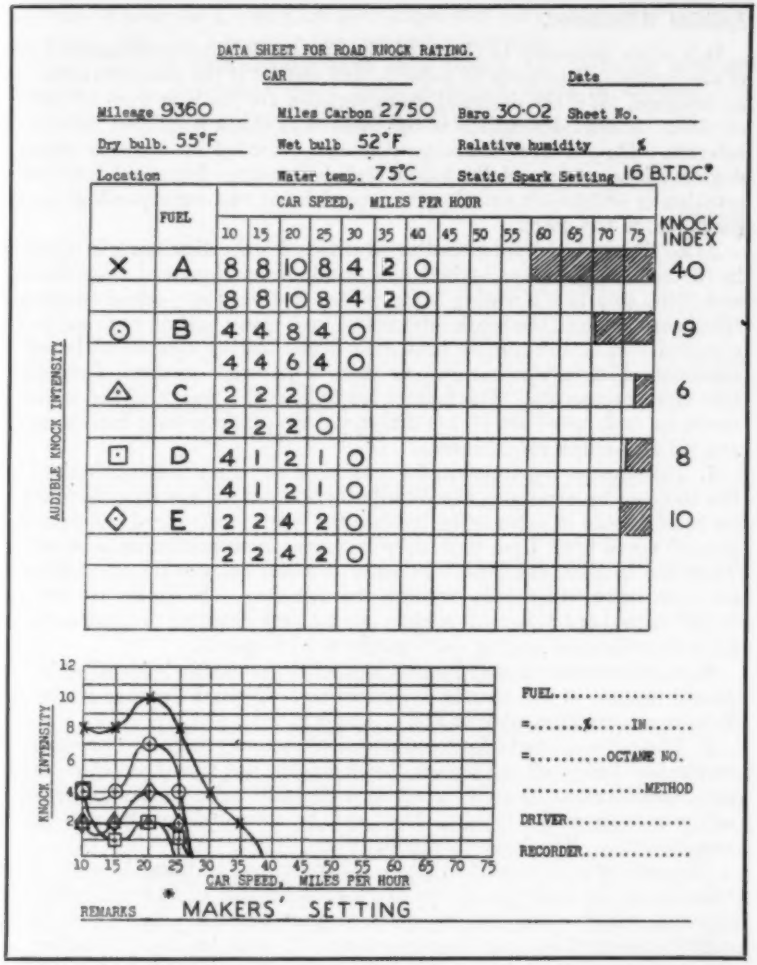


FIG. 3.

too weak or too rich, then the jets have to be changed. With variable jet carburettors it is easy to find the optimum setting from the point of view of performance by carrying out acceleration tests in a manner similar to the ignition tests. It has been found preferable to err on the side of over-richness, even though this may incur a slight increase in consumption,

since too lean a mixture causes knocking, overheating of valves, misfiring and difficult starting. No troubles are experienced from slight over-richness, although a very rich mixture will soot up the plugs and cause a high fuel consumption.

Ignition Adjustment.

It is often necessary to check up the automatic advance characteristics of the ignition distributor in order to find out (*a*) if the characteristics are as designed, (*b*) if the designed characteristics are the best from all points of view. A brief description of the method of check employed may be of interest. The advance characteristics are recorded on a graph relating degrees advance to speed, the former scale being either degrees of distributor rotation or crankshaft rotation, the speed being the corresponding r.p.m. (or m.p.h. in top gear).

As no simple device for recording advance with the distributor in position in the car has yet been devised, the distributor is removed from the car and fitted to a bench testing device which motors it at various controlled speeds and enables the spark advance at each speed and on each car to be recorded. It is unfortunate that such bench testing equipment is rarely encountered at service garages, as there is no other method of checking this vital mechanism. The factors controlling the design of the advance curve for each speed are (1) maximum power, (2) maximum fuel economy and (3) anti-knock requirements.

1. The advance requirements for maximum power are usually obtained on the test bed by arranging the distributor so that the advance may be set by hand instead of automatically, then the spark is advanced and retarded at each speed until 1 per cent. drop in torque from maximum is recorded. Then the ignition equipment designer is asked to provide an automatic advance curve which falls between these limits. The limits are often 5 to 15° (crank) apart, as most engines are not very sensitive to spark advance at or near the peak setting, particularly at high speeds.

Similar information may be obtained after the engine is installed in the chassis by use of the chassis dynamometer. Typical limiting curves for British cars are illustrated in Fig. 4, A and B.

2. The advance curve for maximum fuel economy may also be obtained on the test bed or on the chassis dynamometer, but this is not often taken into consideration in arriving at the automatic advance curve, as more advance is generally required than can be tolerated by the anti-knock requirements. See Curve C, Fig. 4.

The only way at present in which this point can be taken into consideration is by the addition of the extra complication of vacuum-controlled advance, which advances the spark at part throttle only, under which conditions knocking is not experienced. It thus becomes a matter for deciding whether the extra cost and trouble of such equipment is offset by sufficient saving in fuel consumed.

3. The advance curve representing the maximum permissible advance at all speeds for no knock conditions can only be obtained satisfactorily on the road and after 5000 to 6000 miles have been run without decarbonizing the engine, as the thickness of the carbon layer affects the anti-knock requirements by heat-insulating the hot gases from the cooling

surfaces of the head and piston. Excessive carbon formation may raise the anti-knock requirement above that for a clean engine by as much as 8 to 10 octane numbers.

A point which has to be decided before such tests are carried out is the type of fuel on which the car will have to operate in its future life, *i.e.*, whether it is to be a very high anti-knock fuel only obtainable in Great Britain or any No. 1 brand or the cheapest commercial brand.

When the test fuel or fuels have been chosen, the following tests are carried out to determine the "incipient knock curve of advance" or maximum allowable advance without knocking.

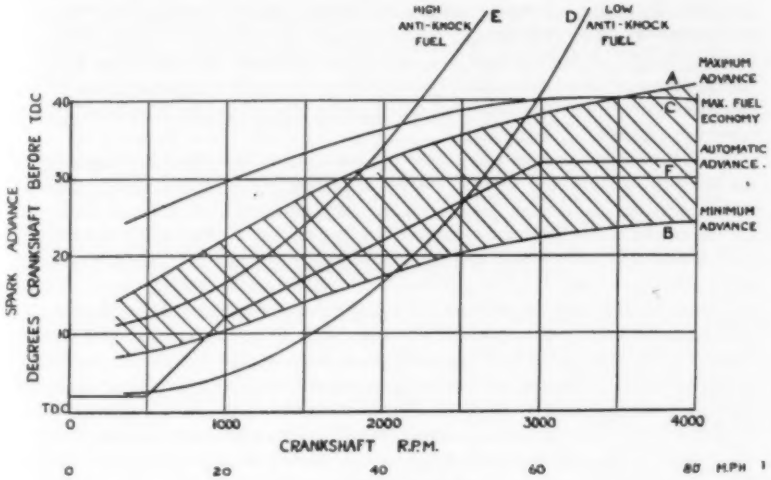


FIG. 4.

SPARK ADVANCE CURVES.

The automatic advance weights are rendered inoperative by wiring them up and a scale is fitted to enable the spark to be advanced in small increments by hand. At each setting the car is accelerated in top gear on full throttle and the speed at which the knock fades out is carefully noted. From the data obtained curves such as D and E, Fig. 4, may be plotted for two fuels. Curve D indicates that the car cannot be operated on this low anti-knock fuel, as insufficient advance can be given to obtain good performance below a speed of 2000 r.p.m., whereas the advance curve E permits an automatic curve such as F to be employed. This curve starts well retarded to permit good idling and safe starting, and then rises as quickly as possible into its working position and continues up to some pre-determined maximum advance.

When this advance curve is settled and the distributor assembled on the car, it is still necessary to take great care in the "static setting," as it is obvious that a faulty static setting will give wrong timing through the whole range of advance.

With regard to spark timing, it has been established, although it is not generally appreciated, that the performance of an engine as shown up by acceleration on the road, is often insensitive to spark timing over a range of more than 10 crankshaft degrees. Also, it is not often realized that in the majority of British cars the performance can be impaired by over-advancing the spark just as easily as by retarding it. The reason for this popular fallacy lies in the fact that at an over-advanced setting the engine runs more roughly, giving the impression that more power is obtained. The small effect of changes of spark advance near the optimum position can best be proved by carrying out acceleration tests against a stop-watch.

On the other hand, the anti-knock requirement of an engine is extremely sensitive to spark advance; thus two degrees retard (crank) may mean a reduction in the anti-knock requirement of 1 to 4 octane numbers. Consequently, an engine may very often be made less fuel-selective without sacrificing any power by simply retarding the spark a few degrees. This practice unfortunately seems to go against the grain in England, but is common practice in America.

For these reasons it is obviously of importance that the static setting of an ignition distributor should be set intelligently and not just advanced until incipient knock is produced on any particular brand of fuel. As an example of this, assume that a car is run on a very high anti-knock fuel which will not permit knocking under any conditions; then if acceleration tests are carried out at gradually advanced static settings, an optimum advance setting may be arrived at. Any retard *or advance* from this setting will cause loss of performance (although it will be negligible for 5°). On changing back to the driver's usual fuel, it may well be found that no knock is experienced; thus he would be gaining nothing by advancing his spark to the incipient knock point. This illustration applies to the majority of British cars on any No. 1 motor spirit. The minority of cars being of the sports high compression type or the badly designed or maladjusted type may knock on No. 1 petrols when set to the optimum setting. Such trouble may usually be rectified by retarding the spark 5 to 10 crankshaft degrees from the makers' setting.

It will be evident that a great quantity of data has been and will continue to be obtained by the petroleum industry, by research institutions and by car manufacturers, and the importance of such research work is being increasingly recognized. It would appear that more rapid and more economical progress is now likely to be achieved rather by refinements in engine design, resulting from such research, than through any spectacular improvement in fuel quality. It is hoped that every manufacturer in the motor industry will recognize the value of such research and will appreciate the endeavours of the Institute of Petroleum and the Institution of Automobile Engineers to further that co-operation between the car and fuel industries which should provide that efficiency in performance which is the common object of both.

SOME FACTORS IN OIL ACCUMULATION.*

By Professor V. C. Illing, M.A., F.G.S. (Member).

Synopsis.

The main purpose of the paper is to consider the influence of texture and buoyancy in the flow of oil and water mixtures through sands and its bearing on oil accumulation.

In order to drive an oil column continuously forward in a flowing water stream within a sand, a definite excess pressure, the forefront pressure, must be exerted within the oil column. This forefront pressure is inversely proportional to the grade size. When an oil–water stream comes into contact with sands of varying coarseness the low forefront pressure of the coarse sand causes the oil to abandon all further movement in the fine sand and to move only in the coarse. Moreover, when the oil reaches the limit of the coarse sand, it is retained there and cannot enter the fine sand until a sufficient pressure is built up within the oil to attain the forefront pressure of the fine sand. This causes the filtration of the oil at the coarse-fine interface.

With regard to directional movement, the function of buoyancy increases the ease of upward oil flushing. An oil–water column in motion must maintain a certain critical concentration. This is less for upward flow than for horizontal or downward flow. Hence when oil has a choice of alternative paths it selects the most upward one, even though it may mean a movement transverse to the main fluid movement. The result is a differentiation of oil from the main water stream and the production of an oil-pool. The application of this idea to various geological structures is discussed.

In a paper on oil migration read before the Institute some five years ago,[1] the author attempted to clarify the issue by separating the processes of migration into two separate stages. The process of enrichment of the reservoir rock at the expense of the source-rock, which was termed primary migration; and the subsequent readjustment of the oil and gas within the reservoir rock, which was termed secondary migration.

It would be easy to criticize any such attempt to subdivide a set of natural processes into various compartments, for nature is usually complex and her methods interdovetail into one organic whole. These processes of migration are by no means an exception. One might argue, with every justification, that there are cases where the reservoir rock and the source rock are one, and that in such cases primary migration is unnecessary, and also indistinguishable from secondary migration. There would be equal justification in the assertion that both stages of the movement were so intimately interlocked in the filling of a sand lens with oil and gas that it is impossible to draw a hard-and-fast line between them.

In spite, however, of these difficulties, there is a distinct advantage in separating the two stages of migration in order that attention may be directed to fundamental differences in the difficulties involved. In primary migration it is the movement of oil through a normally impervious rock and its retention in the porous rock which is the main problem. In secondary migration our attention is focused on movements of separation between the gas, oil and water in the permeable rock, whereby the oil and gas are concentrated in certain portions of the rock to become commercial oil and gas fields. This is a process of segregation and enrichment, one

* Paper presented for discussion at the One Hundred and Eighty-sixth General Meeting of the Institute of Petroleum held on 14th February, 1939.

might almost say a cessation of further movement, quite unlike the first processes of migration.

Many causes have been suggested for the processes of primary migration, such as gravitation, compaction, diastrophism, hydraulic currents, capillarity and surface adsorption. The author has given elsewhere his reasons for considering that most of this primary migration takes place during compaction, and is probably helped by fluid movements associated with diastrophism. It is essentially the outflow of fluids from the compressible rocks, and the oil and gas are entrained in a current of water. The trapping of oil in the reservoir rock is ascribed by the author to the selective filtration of oil and gas from the fluid currents as they pass from the coarse to the fine rocks. This results from the inability of the oil to re-enter the water-wet fine rocks without the development of a considerable pressure differential. This process of selective filtration is essentially associated with interfacial tension, for it depends on the presence of two or more immiscible liquids. It is not, however, a force due to surface tension. One may regard it as Versluys did, as a retention of oil in the coarse sand owing to the excess energy required to develop the much larger surface area of the oil–water interface in the finer rocks.[2] On the other hand, the author prefers to concentrate attention on another aspect of the phenomenon by stressing the required pressure differential. This is a measurable physical phenomenon which definitely prevents oil from entering the water-wet fine rocks. None the less the two views are closely related in so far as they interpret surface tension as a guide, and not as a cause of movement.

The ultimate causes of primary migration are still a fruitful cause of discussion, but as the author's purpose in the present paper is to consider certain aspects of the flow of oil and water in the reservoir rocks, the temptation to linger over the earlier aspects of the phenomena must be avoided.

Physical Relations of Oil and Water in Sands.

It will be sufficient for the present to agree that within the permeable rocks there are fluid movements of water, oil and gas. The extent and velocity of these movements are unknown, but that there is a certain amount of movement will be accepted by everyone save the few who demand a strictly *in situ* origin for oil and gas.[3] Even a cursory study of oil accumulations cannot fail to bring out the importance of their relations to the texture and attitude or structure of the reservoir rocks, and it is therefore reasonable to allow a considerable amount of local segregation even if we decline to accept broad regional migration. For this reason the writer proposes to consider in detail certain aspects of the behaviour of oil–water mixtures in sands, in order to deduce some general principles.

The choice of a two-phase mixture rather than the three phases of gas, oil and water is deliberate, in order to simplify the issue, although the action of gas would have to be considered in a complete review of the whole processes of segregation. This paper is not intended as a complete review, but is rather an attempt to establish principles. Sand is chosen as the typical reservoir rock, as it is convenient and simple to handle. It does not possess all the attributes of every type of reservoir rock, in so

far as it is lacking in joints and other fissure planes, but its porosity and permeability make it an ideal medium for holding oil and water.

The pores within such a medium are neither uniform nor are they separate; it is the grains of sand which are separate. The pores represent a continuous interspace of variable dimensions in which each void space between the grains is in communication with contiguous voids. There is thus a great flexibility of choice of path for any fluid moving in this void space. This distinction is important, and must be continuously borne in mind as an essential difference between the pore system of a sand, on the one hand, and a bundle of capillary tubes, on the other. Another important difference between these two forms of capillaries is that the pores in a sand are roughly triangular in cross-section, and of inconstant dimensions, whereas the normal capillary is circular and more or less uniform in cross-section. As indicated above, these differences lead to a much greater flexibility of intercommunication within a sand than could occur in a bundle of capillary tubes, and it is in some respects fallacious to apply the principles of a normal capillary tube to the pore space of a sand. A single instance will suffice to illustrate the difference. The blockage of a capillary at one point would completely eliminate that capillary from all fluid movement along its entire length. The blockage of a single void between sand grains would cut off none of the contiguous voids from general fluid movement, and its effect would be infinitesimal. It is only when blockage becomes widespread that the permeability of a sand suffers.

In spite of this freedom of intercommunication in sand bodies, gas, oil and water interspersed in a water-wet sand will not separate out by gravitation. The surface tensional features at the oil–water interfaces are sufficient to maintain the separate oil bodies in position unless the sand is so coarse that the capillaries are about 2 mm. in diameter—*i.e.*, the sand becomes a grit. The presence of gas tends to help the process of flotation owing to the greater density difference between gas and water and the tendency for gas and oil to become attached to each other where they make contact accidentally. Even this, however, will not produce flotation in normal sands. Experiments which claim to have produced such movement have in fact involved the production of local pressure gradients within the fluids by the generation of gas within the medium.[4] It was these pressure gradients which induced the movement, and the gas globules, being sensitive to pressure changes, were the main medium whereby the pressures tended to equalize.

Most students of oil accumulation agree that there are two fundamental characteristics of a reservoir rock which appear to control the position of the oil. The first is its texture. Many a large oil-pool owes its occurrence entirely to the presence of a zone of coarse sand in fine sand or of sand in clay. The water-bearing finer sand may be just as porous as the coarse sand, the only difference is that the pore spaces are smaller and more numerous. The second important difference is the attitude of the zone of porous rock to the surrounding and more impervious media. This may be summarized by the implications of the term " closure," which really means a porous zone covered by impervious material and from which no escape is possible without downward movement of the enclosed fluid. Most favourable oilfield structures present a condition of closure in one form or

another, although in some cases the closure is disguised. The logical conclusion to be reached from this is that gas and oil must seek the highest position they can occupy. It would seem obvious that gravitational separation would be a simple explanation of this condition, but we have noted already that this explanation cannot be accepted. It will therefore be necessary to consider the behaviour of oil in flowing conditions to provide an alternative explanation, and in the following sections the author proposes to consider the effects of texture and the direction of flow on the segregation of oil from water.

Effect of Rock Texture.

It is a well-known principle of oil accumulation that the coarser portions of a reservoir rock tend to contain the oil, whereas the finer portions are more commonly saturated with water. This cannot be a question of porosity in the case of sandy reservoirs, for a fine sand is just as porous as a coarse sand, sometimes even more so. Nor can it be due to selective surface adsorption, for the sands are composed of the same material. Surface tension also cannot be the driving force, for experiments show

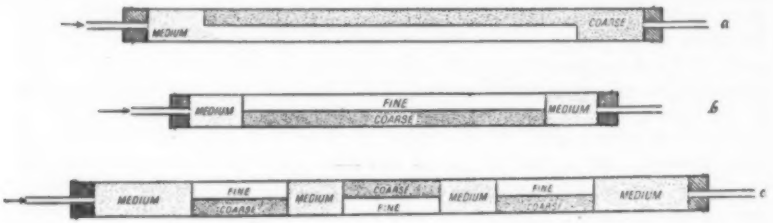


Fig. 1.

that oil globules in water-wet sands tend to resist movement by virtue of surface tension.

If we adopt the principle of selective filtration [1] whereby oil can pass into but not out of a coarse sand which is water-wet, we have a fundamental reason why the coarse streaks should be oil-bearing. One could conceive a set of fluid currents passing along sands of different texture and drifting oil in small quantities with the water. There could be no hindrance to oil passing into the coarse sand, but once it was there, it could not readily pass out again, and so the coarse sands would act as adsorbers of oil from the flowing stream of water and oil. Such was the author's first conception of the process of oil segregation in coarse sand streaks.

In the course of a set of experiments to illustrate this segregation it was at once apparent that this was not the complete explanation. There was clearly a process of path selection in all such movement, whereby the oil, when given the option of a passage through sands of different coarseness, invariably chose the coarser of the two to the complete exclusion of the finer, so that the oil and some of the water passed along the fine sand, while the fine sand contained only flowing water.

In the experiment referred to above, sand was sedimented into a water-filled tube according to the pattern shown in Fig. 1*a*. The sands chosen

were each of one grade, and care was taken in the filling to prevent any streakiness in the texture such as is prone to arise in sedimentation. The two sands were deposited simultaneously, using a moving celluloid strip to guide the deposition, and compaction was ensured by continuous gentle vibration. Gauzes were placed at the ends of the sand column to prevent sand from entering the inlet and outlet tubes.

The tube was placed horizontally and a slow current of water containing about 10–20 per cent. of oil was passed in.

The oil distributed itself fairly uniformly across the section of the tube in the medium sand until it approached the position where the coarse sand had been inserted on half the section. There were now two paths offered to the oil and water, and the oil front immediately began to move more rapidly in the coarse than in the medium sand. This process of selective movement rapidly developed into a complete cessation of oil movement in the medium sand, all the oil passing along the coarse sand streak. When the oil reached a position opposite the end of the medium sand, it rapidly spread to cover the whole of the cross section of the tube, the end of the medium-sand section causing no shadow.

In the first experiment the coarse sand lay above the medium. In order to demonstrate that the result was not due to buoyancy, the experiment was repeated with the position of the sands reversed. The results obtained were identical; the oil chose the path along the lower coarser sand and completely abandoned the upper finer sand after it had advanced less than 1 cm. in the latter. In both experiments movement of water continued in the fine sand throughout the experiment, whereas the fluids moving in the coarse section were a mixture of oil and water.

Experiments were repeated with different arrangements of sand bodies which are illustrated in Figs. 1*b* and 1*c*.

In the experiment illustrated by Fig. 1*b* three sands were used. That of the intermediate grade was placed at the two ends, and the coarse and fine were laid in two contiguous sheets in the middle. The experiment in this case brought into play the function of the coarse–fine interface of the medium to fine sand. The result was that no oil whatever penetrated into the fine sand, but that it all chose the path of the coarse sand. When the oil had reached the end of the coarse sand it was held up at the coarse–medium interface, and the coarse sand was progressively enriched backwards by the displacement of water out of the coarse sand. The water escaped partly at the end of the coarse sand, but also at the junction of the coarse to fine sand along the middle section of the tube.

In the last experiment of the series the sand column was broken up as shown in Fig. 1*c*. The resulting pattern produced a series of coarse and fine lenses separated by medium sands. The lenses were arranged to alternate in position, and the resulting oil flow and oil enrichment produced the result depicted in the diagram. In each case where the oil reached the end of the coarse lens a temporary halt occurred in its frontal flow, and the coarse sand lens became richer in oil. This process continued until the coarse lens contained about 70–80 per cent. of its pore space filled with oil. The oil then broke across the coarse–medium interface. In no case did oil penetrate the fine sands, although water movement continued in them throughout the experiment.

The previous experiment was repeated with the fluids reversed. The sand was carefully dried and then sedimented into the tube in oil. A fluid stream of oil containing 15 to 20% of water was passed through the tube. It was found that the water in this case chose the path of the coarser sand and became trapped in the coarse lenses. Thus it is clear that neither viscosity nor the absolute surface tension of the two fluids could be the determining factor in the segregation of the two fluids.

The experiments were carried out with distilled water, and oil of a viscosity of 11·5 centipoises at 21° C. The type of oil, however, varied considerably in the different experiments. Generally only moderate velocities were used; if the velocity was greatly increased by the use of high-pressure gradients, it was noted that the clear-cut concentrations of the oil in the coarse chambers did not occur, although the travel path still followed the coarse sands.

In order to study the cause of this path selection and the restriction of the oil current to the coarser sand, it was decided to carry out an experiment in which the pressure gradients of the respective water and oil–water columns could be separately measured. Experiment 1*b* was repeated using, however, a tube with manometer connections arranged as in Fig. 2, and three sands were introduced as shown in the diagram. Gauze caps were placed at the entry to the manometers to prevent sand flowing into them, and the tubes were kept as small as possible in order to reduce the necessary flow of liquid to cause the registration of pressure changes within the manometers. The manometer leads extended horizontally from the main tube, and the plane of partition between the coarse and medium sands was vertical.

As usual, the tube was filled by sedimentation, so that originally all the sands were water saturated. A current of water with approximately 20 per cent. of oil was slowly passed into the tube, and the pressures in the manometers were noted as the oil column moved forward to the end of the tube.

The observations are plotted in Fig. 2 in terms of the excess pressure of each manometer above the reading of the outlet manometer.

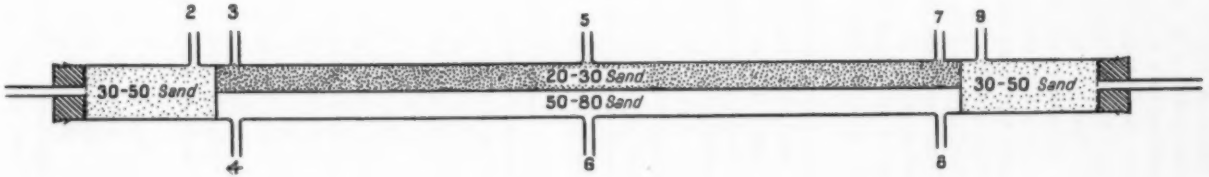
The following points should be noticed:

(*a*) The rapid rise in pressure occurring in manometers 2, 3, 5, 7, and 9 when the oil reached the position opposite the respective manometer.

(*b*) The pressure increases of manometers 2 and 9 were similar, as were also those in manometers 3, 5 and 7. The rise in the former was greater than in the latter group.

(*c*) There was no corresponding rapid increase in manometers 4, 6 and 8 when 3, 5 and 7 rose respectively. The rise in 4, 6 and 8 was more gradual, taking place after the corresponding rise in the opposite capillary.

The experiment suggested that there must be a forefront pressure differential when an oil–water column advanced into a water sand, and that this was an inverse function of the coarseness. This threw a new light on the behaviour of oil in passing through sands of different texture, and it gave a simple explanation of the restriction of oil-flow to the coarse sand.



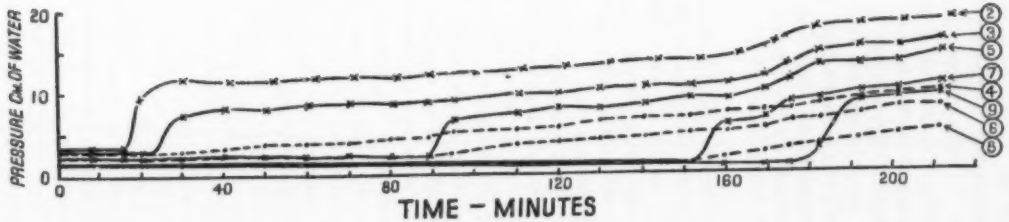


FIG. 2.

THE PRESSURES PLOTTED ARE THE DIFFERENCES BETWEEN THE READINGS OF A GIVEN MANOMETER AND THOSE OF THE MANOMETER ON THE OUTLET TUBE.

To this pressure drop is given the term forefront pressure, and it is clearly a measure of the excess pressure within the oil patches in the advancing fluid measuring the pressure required to continuously deform the fronts of the advancing oil lobes as they penetrate the capillaries. Searching the literature, it was noted that what appeared to be a similar phenomenon had been described by Bartell in 1928, and had been termed by him "Displacement Pressure." [5] In Bartell's discussion of the phenomenon he ascribed it partly to adsorption or to the actual wetting of the mineral matter by the displacing fluid. In the cases which we were examining no such adsorption was taking place, and it was decided to retain for the time being the term forefront pressure, particularly as it was practically self-explanatory. Should, however, it be found later that the two phenomena are identical, Bartell's term would have priority.

Experiments were carried out to study the relations of this forefront pressure differential to the grade of sand and other possible factors (Fig. 3).

The tubes were filled with sand of a uniform grade and a series of manometers spaced along the length of the tube were used to study the pressure conditions in the oil–water column as it travelled past them. The ratio of oil in the inflowing current could be altered at will, and the whole throughput was controlled to maintain a uniform rate of flow of total fluids throughout the experiment.

The pressure rise was shown in each group of manometers, and was found to be the same in all cases, irrespective of the proportional feed of oil to water in the inlet tube. The rate of advance of the oil was, however, naturally dependent on the richness of the inflowing fluid in oil, as well as on the velocity of total fluids.

Experiments were repeated with different rates of flow, and provided that these were not abnormally rapid, the forefront pressures were found to be independent of the general pressure gradient within the sand. At high velocities the forefront pressure was difficult to establish. The forefront pressure was also independent of the direction of flow, whether upwards, downwards or horizontal.

The forefront pressure appears to vary inversely as the diameter of the mean grade size. It is a little difficult to obtain the exact mean size of a sand mass of differing grade composition, but in this case the sands used were of the same origin, and they had been carefully screened to grade dimensions in which the upper and lower limit of the grades were approximately in the ratio of 1·6 to 1 in each sand. The size distribution was therefore likely to be uniform in each case, and errors on this account were reduced to unimportant dimensions. A slight but uniform correction was necessary in all manometer readings on account of capillary effects in the manometers.

Fig. 4 shows the experimental results against a computed curve based on the assumption that the forefront pressure is inversely proportional to the mean grade size. The second curve was obtained by using the results for the grade 30–50 I.M.M. as the basis of computation. The agreement between the observed and computed curves appears sufficiently close to justify the assumption that within these size limits the forefront pressures are inversely proportional to the mean grade size.

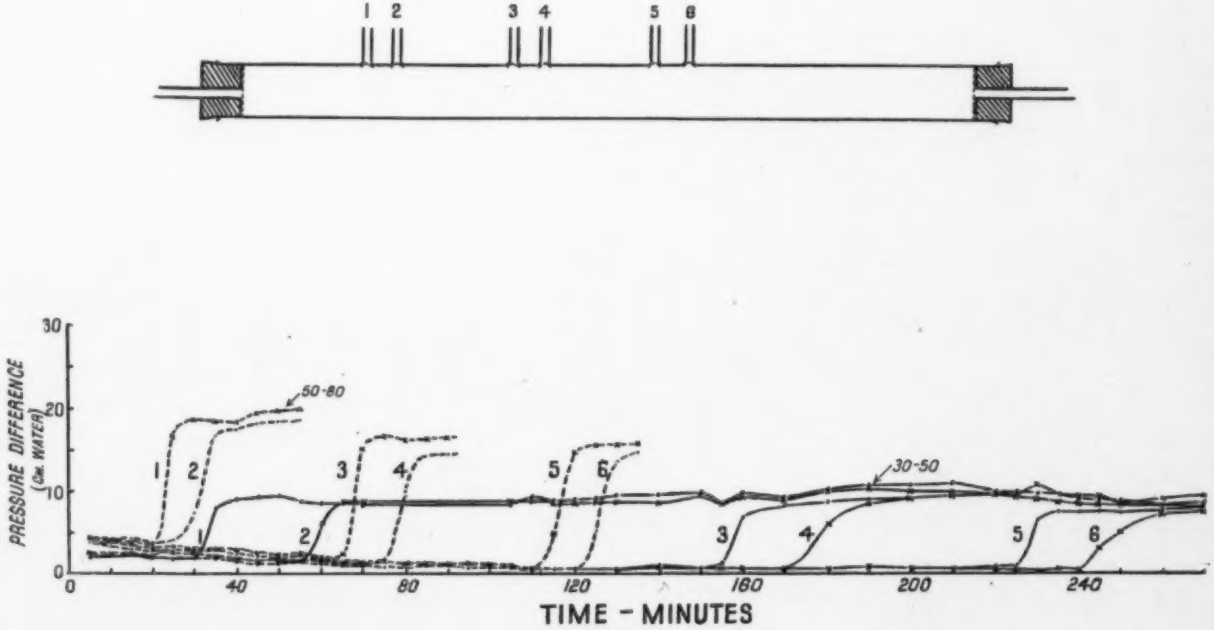


FIG. 3.

THE PRESSURES PLOTTED ARE THE DIFFERENCES BETWEEN THE READINGS OF A GIVEN MANOMETER AND THOSE OF THE MANOMETER ON THE OUTLET TUBE. CURVES ARE SHOWN FOR 30–50 SAND AND FOR 50–80 SAND.

If we assume the validity of this law for silts and clays of finer dimensions, it would appear that the forefront pressure for a silt of 0·1 mm. diameter is 29 cm., and for a particle of 0·01 mm. diameter equivalent to a fine silt the forefront pressure should be about 290 cm. These pressures are not large, but it is probable that the pressure gradients in nature are quite

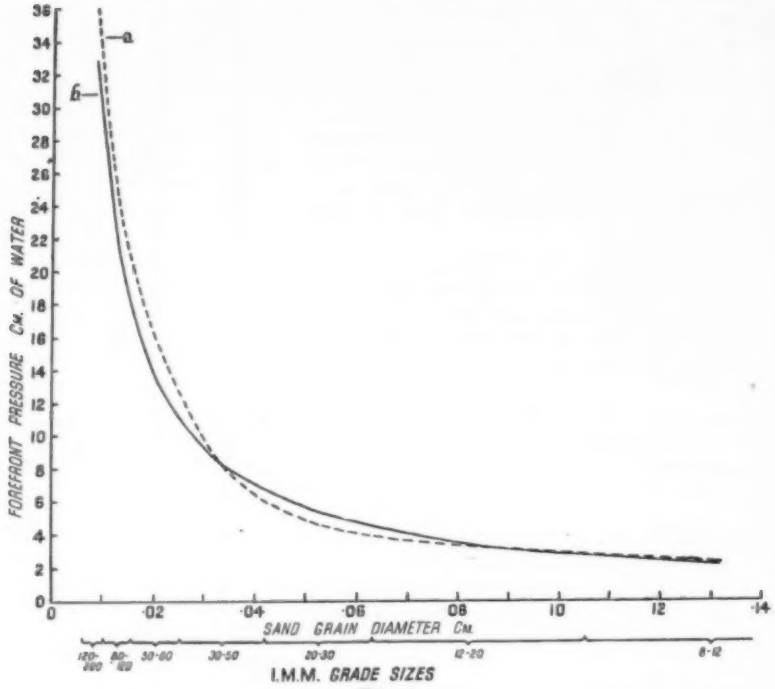


FIG. 4.

a, CURVE OF OBSERVED FOREFRONT PRESSURES, WITH MANOMETER CORRECTION APPLIED USING A VALUE OF 26 DYNES/CM. FOR THE OIL–WATER INTERFACIAL TENSION.

b, CURVE OF FOREFRONT PRESSURES CALCULATED ON THE ASSUMPTION THAT THE FOREFRONT PRESSURE IS INVERSELY PROPORTIONAL TO THE MEAN GRAIN SIZE, AND USING THE EXPERIMENTAL VALUE FOR 30–50 SAND AS BASIS.

small, and such factors as these would be more than adequate to guide oil accumulation.

The existence of this forefront pressure suggested an obvious relation between the selection of the path by the oil and the retention of the oil at a coarse–fine interface. The oil passed into and along the particular sand which allowed it to advance with the least forefront pressure, but it was held up when it reached a fine sand until a sufficient pressure was built up in the oil to reach the necessary forefront pressure of the fine sand. On this assumption the filtration pressure—*i.e.*, the pressure required

to force it across the interface—would be equivalent to the difference between the two respective forefront pressures within the two sands.

In order to study these relations, the following experiments were carried out.

A short tube with two manometers was filled in the normal way with coarse and fine sand in two separate segments. Oil was allowed to enter the coarse sand and the forefront pressure noted in the first manometer. The oil was allowed to continue to advance slowly and the pressure build-up was noted in the first manometer immediately preceding the bursting of the coarse–fine interface. The experiment was continued to give the forefront pressure in the fine sand. The filtration pressure was noted to be the difference between the two forefront pressures.

The results of these experiments appear to confirm the relations between the forefront pressure and the filtration pressure, and the following general conclusions may be reached :

(*a*) A definite minimum pressure, the forefront pressure, is required to force oil into and along any water-saturated sand.

(*b*) The pressure is an inverse function of the radius of the sand particles, and for this reason oil will always select the path through the coarse sands.

(*c*) The pressure is required to maintain sufficient pressure within the oil globules to deform their frontal lobes.

(*d*) The process of filtration of oil at the coarse–fine interface is really a question of the need for a build-up of pressure to attain the necessary forefront pressure of the finer sand.

(*e*) This build-up of pressure can be temporarily avoided by the by-passing of water into the finer sand, leading to the enrichment of the oil body. This will continue until much of the water has been driven out, and the interface will then be broken down.

(*f*) Even after the breaking down of the interface the coarser sands will still be richer in oil than the rest unless continuously flushed with water, and the most difficult zone to flush with water is the coarse–fine interface. The fact has an important bearing on the water flushing of sands, and will mean that where there are numerous textural changes in the reservoir rock, it will be increasingly difficult to obtain a high percentage of oil extraction. All such coarse–fine interfaces tend to lock away oil in the strata.

The experiments have been carried out at normal atmospheric pressures, and it is not suggested that the same quantitative figures would apply at the pressures and temperatures of oilfield strata. However, it is the principle of the process which is important, and from a qualitative point of view there is no reason to doubt that the same processes will occur at high pressures as at low pressures, so long as the oil and water remain liquids.

The above considerations appear to give a satisfactory explanation of the phenomena associated with the textural accumulation of oil. They will need some modification, in so far as the normal oil reservoir often contains free gas as well as oil and water. This will give an additional complication into which we have not yet fully entered, but the principles ought to remain the same.

Buoyancy.

It would seem at first sight that there need be no difficulty about the upward movement of gas and oil in a reservoir rock. In some cases, where the rocks are fissured or where the cavities are large, there is no doubt that gravitational separation occurs, and the three separate media seek their own hydrostatic levels. The capillaries of the normal sand are, however, too small for such separation, and the upward movement of the gas and oil must be explained in other ways.

In a previous contribution to the *Journal* the author described an experiment, in which, under flowing conditions, the action of buoyancy was clearly indicated.[1] Two separate streams of water and kerosine were partly able to cross each other's path in a tube of sand, the water travelling downwards, whilst the kerosine passed upwards. The separation was not complete, but it was quite definite. The results are also in agreement with the experimental work of many other workers, and there can be no doubt that in flowing currents oil and gas will readily move upwards in a sand body, whereas under static conditions the same oil and gas will not rise.

The behaviour of oil and gas in currents of water within a permeable rock is by no means well understood, and even a cursory review of the literature will reveal many contradictory statements on the subject. Some deny that there can be any downward movement of oil and gas, others argue that there must be some limiting angle of dip below which oil will not migrate up dip; whilst still others deny that oil can be flushed along at all by migrating water currents with the velocities which exist under natural conditions. This confusion of thought is largely because most of the experimental work has been qualitative rather than quantitative, and has therefore failed to reveal the many factors which determine the behaviour of oil and gas. It is, for instance, quite possible to perform experiments which appear to support each misconception referred to above, but only because some factor, such as oil concentration, is strictly limited. The fact is that oil and gas can be carried upwards, downwards or in any other direction, but not with the same facility. It is also possible to have a fast current unable to move oil from a sand at one concentration, and a comparatively slow current able to move oil along in this same sand at another concentration. The factors which determine the behaviour of oil under such conditions include the following: Oil–water concentration, forefront pressure, permeability, velocity, direction of flow, and the attitude of the boundary planes of the porous media and the nature of the contiguous material.

Our experiments on the effects of these factors are still incomplete, but sufficient data have been collected to enable us to reach some conclusions on the question of the buoyancy of oil in currents of water.

To realize adequately the problems in oil–water movement it is, in the first place, necessary to visualize the conditions under which the oil exists in the water-wet sand. The water occurs as a film over all the surface of the sand-grains, and also fills some of the pores. The oil forms irregular bodies which occupy one or more large pore chambers and are completely surrounded by water. Each oil patch is bounded by an oil–water skin of variable shape dependent on the walls of the pores. Its external form

under static conditions is therefore dependent upon the constricting pore walls, the oil–water interfacial tension, and the oil's buoyancy. It therefore adopts a form in equilibrium with these three conditions. Should, however, movement be induced in the surrounding water, the pressure gradient set up causes a modification in the form of the oil patch resulting in the reduction of the curvature of the oil–water interfaces on the high-pressure side and increased curvature on the low-pressure side. The extent of this effect will depend on the pore size and the pressure gradient in the water. Since the latter is an inverse function of the permeability and a direct function of the oil–water concentration, it is clear that these two will have a bearing on oil movement.

Should the deformation of the oil cause one of the convex lobes on the low-pressure side to pass through a pore restriction, an immediate change in shape and position of the oil occurs, involving the occupation of a new pore and the retraction from an old one. The movement is spasmodic, not continuous, and is clearly associated with the changing pressures in the surrounding water. The oil moves forward rather like a sinuously-shaped amœba sending out tongues or lobes into forward chambers and retreating from those behind. In doing so the buoyancy of the oil has full scope to play its part, and it does so in the choice of those lobes which will move forward, the upward ones having the preference if other things are equal. If, however, the pressure gradient be a downward one, or if one of the lower pores be larger than the upper ones, the lower oil lobe will be the one to advance. On this principle the oil movement will always tend to be in the direction of the local pressure gradient, but with a bias towards upward movement in relation to the water.

It also follows that oil movement will depend on the pressure gradient, the permeability (coarseness) and the oil concentration. The latter is important, in that it determines the local pressure gradient in the water. The higher the oil concentration the more restricted is the water passage, and the higher therefore becomes the drag on the oil causing it ultimately to move.

In general, the lower the velocity the more is the oil by-passed by the water, resulting ultimately in a higher oil concentration in the material remaining behind. This concentration increases until the local pressure gradient becomes sufficient to force the oil along, the oil–water concentration remaining constant for this travelling zone provided the pressure gradient remains the same. Thus if oil in small quantities is continuously fed into a slow water stream within a sand, it will produce an oil–water zone within the sand which is more concentrated than the inflowing stream.

The principle that oil flushing depends on concentration as well as on pressure gradient implies that at low concentrations of oil in water currents the oil will remain stationary and be by-passed by the water. This feature is common to all sands, and it must automatically limit the powers of transport of a definite quantity of oil by water currents. The oil, if initially concentrated, will merely be distributed along the line of flow until the concentration is sufficiently diffuse to allow continuous by-passing. This occurs under laboratory conditions when the concentration of oil is reduced to about 10–15 per cent. of the total pore space.

The above consideration has two important corollaries. First, to produce continuous forward movement of oil there must be a continuous feed of new oil to the flowing stream, and secondly, if this feed of new oil ceases and forward flushing continues, the oil as a whole will be dispersed rather than concentrated. It is, however, true that a portion of it may be locally concentrated by some accident of texture.

Considerations such as these must be given due weight before we allow unlimited scope to the exponents of widespread regional lateral migration, particularly when we realize that in nature changes in texture are numerous and such textural changes are very important in stopping further migration.

There is no lower limit of velocity at which oil movement will not take place provided the oil concentration is sufficient. In fact in an oil-bearing sand which may still contain some 20 per cent. of water in its fluid content there may be no movement of the water at all, but only of the oil.

Turning now to the question of the direction of flow within a sand body, it is obvious that downward movement of oil in a current of water will always be more difficult than upward movement, because the latter is helped by the buoyancy of the oil, whereas in downward flushing the drag of the water has to overcome the buoyancy factor. If now we adopt the principle set forth above, that for a particular grade of sand and a particular concentration there will be a definite velocity at which oil may be moved, it may be deduced that for upward flow the velocity will be lower than for horizontal flow, and for downward flow it will be higher. Alternatively, this will mean that for upward flushing the oil concentration will not be so high as for downward flushing.

This conclusion that for a particular velocity the critical oil concentration for upward flushing is less than for downward flushing, means that whenever an oil–water stream has the option of two courses the oil will invariably choose the upper to the exclusion of the lower. The only condition in which oil would journey in both directions would be when the oil concentration was much higher than the critical oil concentration for that particular pressure gradient.

Furthermore, it may be deduced that where the oil and water are given a certain liberty of choice of path due to variations in the inclination of the boundary surfaces of the sand, the oil will invariably choose the steepest path, provided the texture of the sand remains constant.

A series of experiments were carried out to test the validity of these deductions. The principle adopted in these experiments was to give the passing fluids a choice of path and to examine their adjustment of oil to water which took place under those conditions.

In the initial experiments oil and water were passed into the mid-point of a vertical tube filled with water-saturated sand in a thoroughly compacted condition. The oil and water inflow could be independently controlled, so that the rate of inflow and the proportion of oil to water could be varied in the experiments. The oil, once in the vertical tube, was free to select its path either upwards or downwards, and the factors which governed this selection could be studied. The liquids were free to escape from both the upper and lower end of the tube, and the rate of flow could be adjusted in each case. In the later experiments the single vertical tube with a narrow inlet tube at the side was replaced by a T-tube in which each limb was of

the same diameter. The stem of the T was used as the inlet tube, and constituted an improvement on the original narrow inlet tube, in that it was wider and less likely to involve accidental bias in the initial direction of flow of the oil when entering the vertical tube. There was, however, no evidence throughout the experiments that any of the results could have been affected by such accidental bias.

In the first experiment the tube was filled with 12–20 I.M.M. sand and an oil–water current introduced into the side tube. The rate of flow and proportion of oil in the inflowing tube were stabilized as far as possible, and the delivery of both the upper and lower outlet was maintained at the same value. It was noted that after a slight movement of 2 cm. downwards all further downward movement of oil ceased at normal velocities (Fig. 5). On the other hand, the upward movement of the oil was continuous. The experiment was repeated using different sands, altered rates of flow and with different proportions of oil in the inflowing stream.

Comparison of results obtained as shown in Fig. 6 indicate that except at high oil concentrations all the oil normally moves upward and most of the water moves downward. The latter result is due largely to the reduced permeability of the oil-filled section of the tube. Downward flow of oil can generally be achieved by increasing the velocity or by increasing the percentage of oil in the inflowing stream. If the results for sands of different grade size are compared, it is noticeable that it is more difficult to cause downward flow in the coarse than in the fine sands.

In the later experiments with the wide T-tube the exit tubes from both the bottom and top limbs were adjusted initially to give the same rate of flow when water alone was passed into the sand. After this preliminary setting no further adjustments were made in the exit tubes, and the flow along each limb was allowed to adjust itself to the conditions within the tube. Fig. 6 gives the results of this experiment, and indicates that very little downward movement of oil could be induced in these circumstances. It is noticeable that as the oil increases in the upper tube a greater amount of water is forced to flow in a downward direction and less water in an upward direction. In some of these experiments the only way in which oil could be forced downwards was by closing the upper tube entirely. At higher concentrations of oil in the inflow fluid it was more easy to induce downward flow of oil.

The experiments were repeated with the flow tube at an angle of 5° from the horizontal, so that the alternative paths offered to the oil-and-water mixture were 5° downwards and 5° upwards. The flow of the two streams was not regulated after the preliminary setting to give an equal flow of water along each limb. Figs. 7 and 8 show the results and indicate the movement of oil along each limb. The importance of the buoyancy factor is again shown in differentiating the flowing current into two streams, of which the upper contains the main quantity of oil and the lower the main water flow.

One further experiment is an interesting example of the textural factor being utilized in opposition to buoyancy. In one of the first experiments (1*a*) it was noted that oil would move downwards rather than upwards if it could take advantage of a sand of lower forefront pressure. To explore this condition an experiment was carried out giving alternative paths of

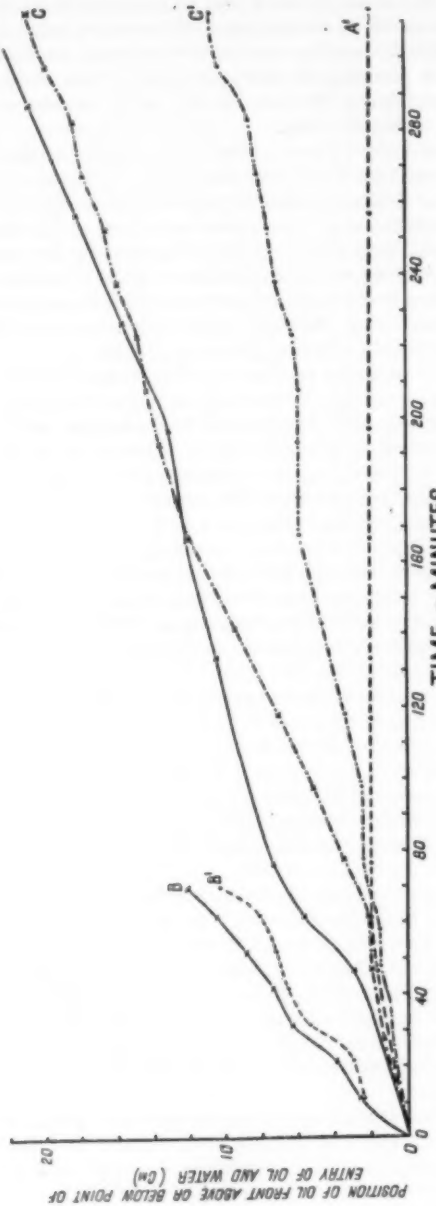


FIG. 5.

CURVES A, B AND C SHOW UPWARD MOVEMENT OF OIL. CURVES A′, B′ AND C′ SHOW CORRESPONDING DOWNWARD MOVEMENT OF OIL.
AA′, 12–20 SAND; MEAN RATE OF FLOW UPWARDS AND DOWNWARDS, 17·8 C.C./HR.; OIL–WATER RATIO, 1 : 8·3.
BB′, 12–20 SAND; MEAN RATE OF FLOW UPWARDS AND DOWNWARDS, 148 C.C./HR.; OIL–WATER RATIO, 1 : 16·3.
CC′, 30–50 SAND; MEAN RATE OF FLOW UPWARDS AND DOWNWARDS, 19·3 C.C./HR.; OIL–WATER RATIO, 1 : 4·7.
DIAMETER OF TUBE, 2·5 CM.

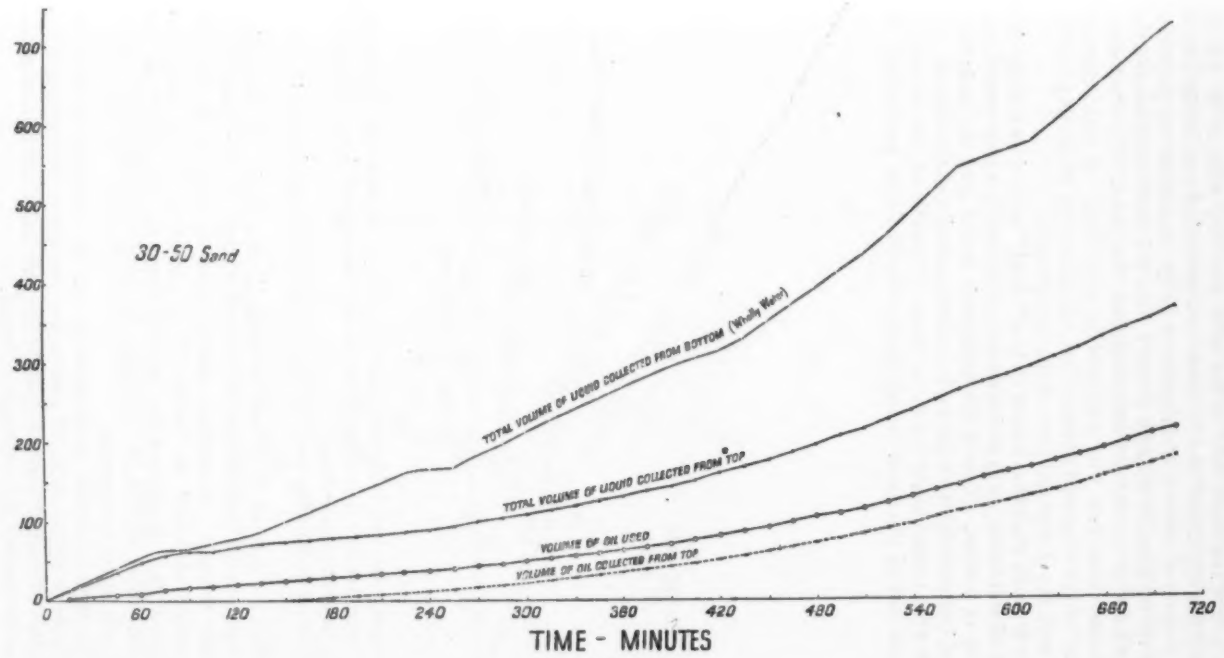


FIG. 6.

DISTRIBUTION OF FLOW OF OIL AND WATER IN SHORT VERTICAL SAND-FILLED TUBE, THE INLET TUBE BEING OF THE SAME DIAMETER AS THE VERTICAL PART. THE FLOWS WERE NOT CONTROLLED AFTER THE INITIAL ADJUSTMENT TO EQUALITY WHEN WATER ONLY WAS BEING INTRODUCED.

flow in a T-tube the lower limb of the tube was filled with 20–30 I.M.M. sand, whilst the upper limb and the inlet tube were filled with 30–50 I.M.M. sand. A current of water containing about 20 per cent. of oil was passed in, and when the oil reached the fork of the T-tube it immediately entered the coarser sand and proceeded downwards against buoyancy. The experiment was continued until flow was stabilized in each limb. A small amount (4 per cent.) of the oil passed upwards into the finer tube, whilst 96 per cent. of the oil took the downward path of the coarser sand.

In order to study the behaviour of oil in a " dead " zone close to a moving column of oil and water, an experiment was carried out in a four-armed tube in the form of a cross. Two of the arms were sealed, and the main limb was placed horizontally with the sealed arms upward and downward. Oil and water were passed along the main stem. It was found that oil tended to segregate out of the main stream in the closed limbs, particularly in

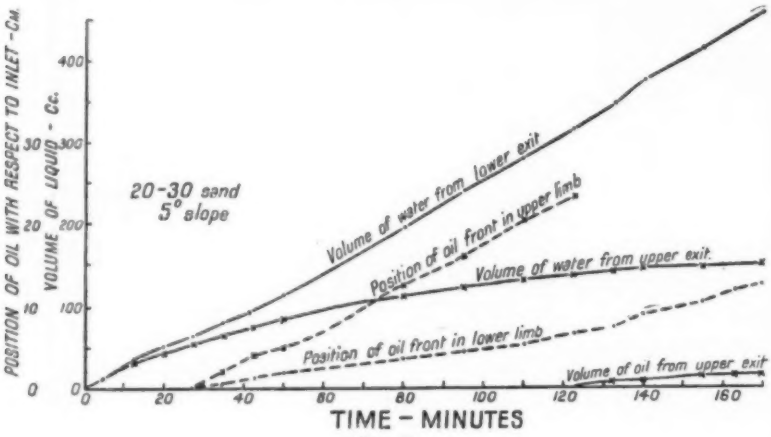


FIG. 7.

the upper one. On revolving the tube in order to reverse the limbs, the main oil concentration was transferred to the new upper limb, which had previously been the lower one.

The following deductions may be made from these experiments:

(*a*) Where a current of oil and water is given a choice of alternative paths, one upward and the other downward, there is a differentiation of the two streams. Around the critical concentration of oil—*i.e.*, the concentration at which oil flushing is just possible for the particular velocity—all the oil chooses the upward journey. At higher oil concentrations most of the oil continues to move upwards, but a small amount will move downwards.

(*b*) The differentiation is dependent on the velocity, coarseness, difference in densities of the oil and water, and the concentration of the two fluids. Differentiation is helped by low velocities, low oil concentration, low oil density and coarseness of sand.

(*c*) Where the oil–water stream is presented with paths of varying gradients, the oil invariably chooses the most upward path possible. This choice is again helped by the same factors as in (*b*).

(*d*) Where a dead zone, or zone of low-pressure gradients exists, an oil–water stream tends to feed this zone with oil, and concentration of

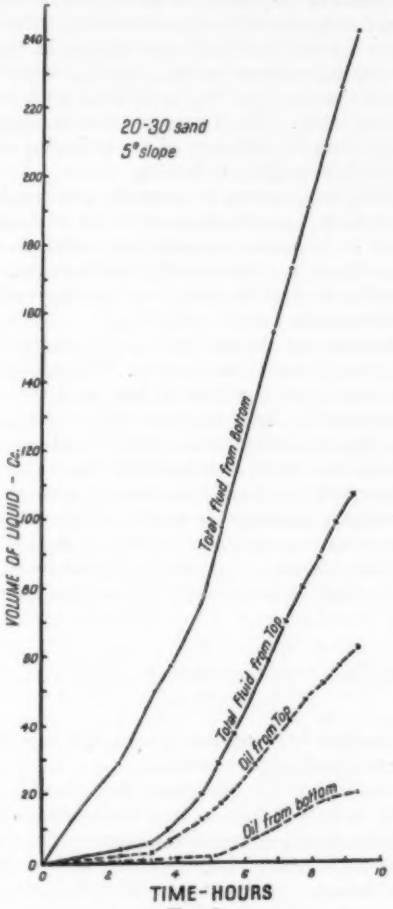


FIG. 8.

the latter takes place. This is particularly true if the " dead " zone occurs in a high rather than a low position.

These general conclusions, based on experimental results, are also in agreement with theoretical deductions, for if it be agreed that oil flows upwards in a water current more easily than downwards, and, secondly, that by-passing is a function of grade, velocity and oil–water concentration,

then the differentiation of oil from water in flowing conditions which can be achieved only by by-passing, must also depend on concentration, velocity and the attitude of the sand, as well as on the density difference between the oil and the water.

It appears therefore that the first stage in oil accumulation in a sand body is achieved by the gradual by-passing of oil by the current of water until the oil concentration has been sufficiently enriched to attain a concentration wherein it can move forward without any change in this concentration. This is termed its critical concentration. Such a mass of oil and water can move forward continuously so long as it is fed with oil and water, and will retain its concentration. The degree of concentration will depend on the forefront pressure and the richness of the inflowing oil–water mixture and the velocity at which the fluid is flowing.

The second stage in enrichment is normally produced by a change in texture, and results from the filtration effect at a coarse–fine interface. This can result in an enrichment to a sand containing about 80 per cent. of its pore space filled with oil and the rest filled with water. This is probably as rich a concentration as ever occurs in oil-bearing rocks, save those of very coarse texture or under fissure conditions.

An alternative second stage in enrichment may be produced by changes in the direction of flow of the oil and water. Where the flow is upwards, the critical oil concentration for flow is less, and the oil–water stream becomes less concentrated, but, on the other hand, it moves much faster. Where the flow is downwards, the critical oil concentration for flow is higher, and so the oil stream must become denser to achieve any movement. On the other hand, such movement is slower and much more difficult. Hence when a flowing oil–water stream increases its upward gradient and then diminishes it, there will be an enrichment of oil at the position of diminishing gradient. A similar enrichment is possible where changes occur not in the inclination of the flow, but in the amount of the pressure gradient.

Some Examples of Structural Accumulation Based on Buoyancy.

It will be interesting to consider the application of some of these principles to actual oil-field accumulations.

So far as the textural feature is concerned, little need be said to emphasize its importance, for it is well known in all oil-fields where the reservoir rocks vary in texture, that in general the coarser streaks are those which are oil bearing. Some of our major oil-pools can be described as nothing more than inclined lenses of porous reservoir rock in which the oil and gas occupy the upper part and water fills the rest of the body. Here the accumulation appears to have been brought about by migration into the sand lens and filtration at the coarse–fine interface at its upper end. East Texas and Midway Sunset fields are examples of this type.

Within many fields the oil–water distribution may be found to be extraordinarily complex when the sand bodies are composite. Whilst faulting and fissuring undoubtedly play a part in such complexity, the variation in grade composition is nevertheless a main contributory factor.

It is, however, to some of the structural features that the author wishes to direct attention. The anticline will immediately be called to mind as the striking example of the buoyancy principle. Accumulation of oil in anticlines is, however, a very complex subject. To treat it adequately would need a paper of much greater scope than is intended. The author proposes to consider only a few types of structures of simple form which are recognized as oil-traps, and to discuss the features which in his opinion tend to favour the accumulation of oil. The three examples have been chosen to illustrate the principles set out in the earlier part of the paper.

Structural Terraces.

Perhaps the least definite of all structures which have been claimed as favourable for oil accumulation are the structural terraces. Their value was first noted by Edward Orton, who spoke of them as arrested anticlines. They may be described as local flattenings of the dip on a general monocline, and as they do not have any dip reversal, there is no definite closure to explain the oil concentration. This lack of closure has led many geologists to cast doubt on the validity of the structural terrace as a cause of oil accumulation,[6] and indeed it cannot be claimed that the recent developments in oil discovery have strengthened the claims of the terrace to recognition. Yet we cannot dismiss the terrace and its first cousin the monoclinal nose as of no importance, and their value requires explanation.

The normal explanation of the terrace is that the flattening of the bed provides an area on which the dip is too low for upward oil migration. Hence the oil being carried up the monoclinal dip comes to rest on the flattening, and remains there. This explanation appears to infer that oil cannot be carried along a flat bed, which we know is untrue. The author's chief criticisms, however, of the orthodox explanation of the terrace is that it falls far short of the full story. His conception of accumulation on the structural terrace and monoclinal nose is likewise based on the supposition that they are due to the migration of oil and water up dip. The most important feature is, however, not necessarily the flattening of the dip, but rather the zone of abnormally high dip which must always exist just below a terrace or monoclinal nose. This zone of excess dip—*i.e.*, a dip which is above that of the general average dip of the monocline—is the counterpart of the flattening, and brings the general structure below the terrace into line with the general monocline (Fig. 9*a*).

The oil–water current which approaches this zone of increased dip is partly differentiated as explained in the previous section. The oil tends to be focused towards the terrace, choosing the path of the maximum gradient. This automatically means that the oil–water mixture which arrives at the edge of the terrace is enriched in oil.

The fluids which flow onwards over the terrace cannot carry out this proportion of oil, and water is bled out in preference to oil, leading to a second cause of enrichment of oil on the terrace. Thus oil is being brought in at abnormally high rates to enrich the concentration, and is being carried out at abnormally low rates. The result is a continuous enrichment, and the creation of a mass of oil, which owing to its viscosity aids as a general block to the migrating fluids. Such a block or dead zone on the

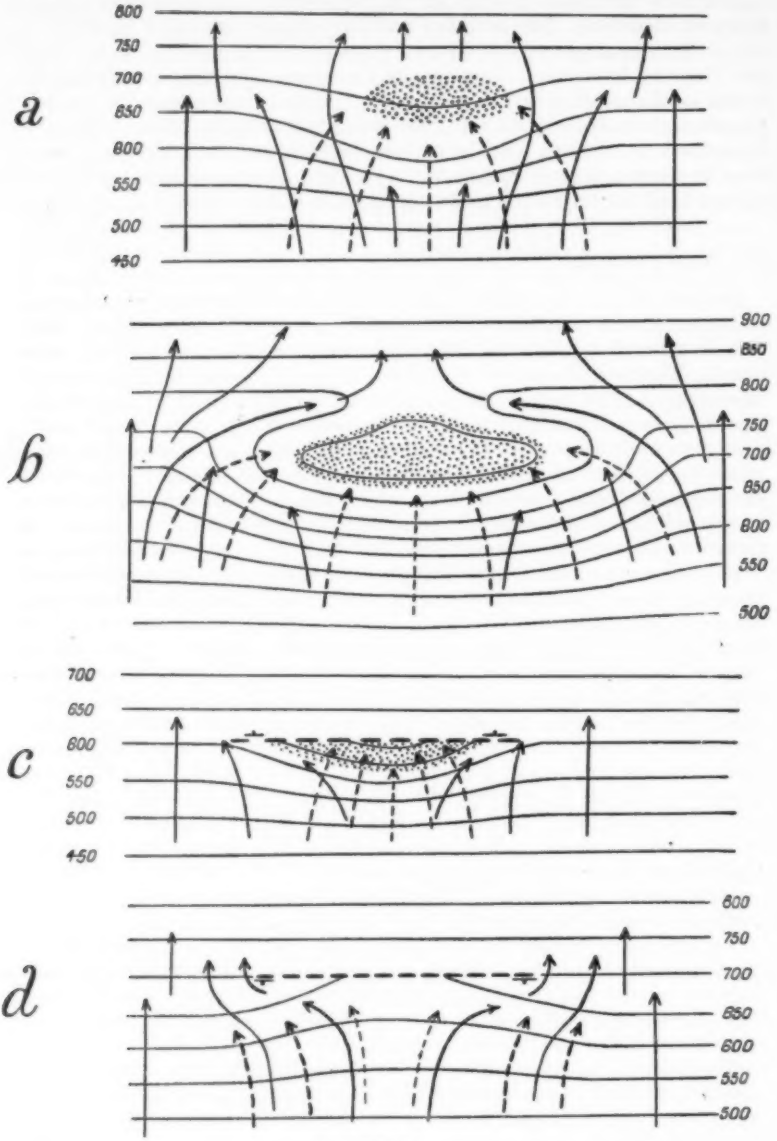


Fig. 9.

FULL ARROWS, CURRENTS CONSISTING MAINLY OF WATER. BROKEN ARROWS, OIL-ENRICHED WATER CURRENTS. DOTTED AREAS SHOW OIL ACCUMULATION.

flattening of structural terrace acts as a back eddy in which further oil accumulation can take place.

Monoclinal Domes.

The simple explanation of the monoclinal dome as a trap for up-dip migration has perhaps required modification in some instances since the discovery of the relations of some of these structures to buried ridges. More particularly is this true of those cases where vertical migration may have played an important part in the oil accumulation. On the other hand, there seems good evidence in most cases to favour at least some amount of regional migration, and in such cases the mode of accumulation would be on the same lines as that of the terrace. Again attention should be directed in the first place to the steepening below the dome and the way the regional stratum contours must bend around the structure focusing the oil enriched stream towards the dome (Fig. 9*b*). Again, the outflowing current from the dome, being downward, would be deprived of its oil. This would result in the enrichment of the dome in oil and gas at the expense of the migrating fluids. The dome would gradually become a zone of the more viscous oil—in other words, a dead zone in the general pressure gradient, and would then be fed with more oil on its lower side by up-dip migration.

Fault Structures.

Perhaps one of the most important applications of up-dip migration and the trapping of oil by the alteration of the dip of the beds is given in the case of fault structures. It is generally agreed that strike faults are the important trap structures, and that their effect is dependent on closure. On the other hand, it is not sufficiently emphasized that the majority of such fault-traps which have been responsible for oil accumulation are those in which the downthrow is on the up-dip side. Thus along the Balcones fault system it is the supplementary faults with downthrows on the north-west side, not the main fault with the throw in the dip direction, which are the oil accumulators. Even the suggestion that the supplementary faults have screened the oil from the Balcones fault is not satisfactory, for there are gaps in the secondary fault system, and quite considerable feeding-grounds for the main fault.

If, however, we examine the structure contour system, which must in principle occur in association with these two types of strike faults (Figs. 9*c* and 9*d*), we note that in the case of the faults which are upthrown on the down-dip side the regional dips near the fault will focus oil towards the fault plane, whereas in the case of the faults with the downthrow in the dip direction the regional dip will have no such focusing tendency. Thus, in spite of the fact that both faults may produce the same actual blockage to fluid migration as a whole, the fluid which accumulates in the case of the favourable fault structure is more highly oil enriched than in the case of the other fault.

There exists, of course, in the case of faults other complications, such as associated warping of the strata, dip faults and zones of vertical migration, and the author does not wish to suggest that the preceding analysis is more than a partial one, but it is useful in its suggestion that

the structure approaching a fault may be just as important as the fault itself.

The author wishes to emphasize that these three examples are put forward merely to illustrate the application of the principle that oil always chooses the steepest angle of flow up-dip that it can attain. The treatment is meant to be suggestive and no attempt is made to make it complete.

Conclusions.

In conclusion it will perhaps clarify the position if the broad conclusions of this paper are divided into two sections: (*a*) the physical principles involved and, (*b*) their implications with regard to the process of oil accumulation.

(a) *The Physical Principles.*

(1) A flowing mixture of oil and water in a sand body consists of separate lobes of oil completely surrounded by the water medium. The movement of the two liquids is largely independent. That of the water is continuous, whilst that of the individual oil lobes is spasmodic.

(2) A definite forefront pressure is required to force oil into a water-saturated sand. This forefront pressure is greater than the pressure in the contiguous water, the difference being an additive factor due to interfacial tension between the oil and water.

(3) This forefront pressure is inversely proportional to the mean grade size of the sand.

(4) When an oil–water column advances, there appears to be a necessary minimum or critical concentration of oil within the sand before the oil can be moved forward. This critical concentration is dependent on the sand grade and the pressure gradient.

(5) The existence of a critical forefront pressure for each grade of sand involves the consideration that oil will not penetrate from a coarse to a finer sand if both are water-wet, until the pressure in the oil column has been built up to the forefront pressure of the corresponding fine sand. This build-up of pressure corresponds to what the author terms the filtration pressure of the coarse–fine interface.

(6) Oil–water movement in a sand is affected by the forefront pressure, permeability, the oil–water concentration, the pressure gradient and the direction of flow.

(7) The buoyancy factor in oil renders it more easily carried upwards than downwards or horizontally; this results in a predilection for upward flow and causes the oil to separate upwards in a flowing oil–water stream. Under static conditions there would be no separation of the oil and water.

(8) The textural separation of the oil from the water is not due to the fact that water has the higher surface tension and thus goes to the finer sands. If the sands are originally oil-wet, the two liquids can be reversed. The whole process of separation is, however, guided by the forefront pressure conditions, which are the result of the interfacial tension of oil and water.

Application of these Physical Principles to Oil Accumulation.

(1) Oil accumulation is guided very largely by texture and all oil movement tends to be in the coarser rocks.

(2) The oil is trapped, and much of the water is filtered out at the coarse–fine interface—*i.e.*, at the upper surface of the coarse streak. So we have oil sands in clays, oil-bearing coarse sands in water-bearing fine sands.

(3) Whenever the dip of a potential reservoir rock is locally increased oil tends to be focused from the oil–water migrating fluids. Whenever the dip decreases, the flow of oil across such a flattening is hindered. Hence we have the oil accumulation on monoclinal noses, terraces, etc.

(4) A reversal in the regional dip is an excellent trap, because down-dip oil movement is possible only at high velocities or at high concentrations of oil. Since the former are very unlikely in nature, it means that a high oil concentration must be formed on a monoclinal dome before the spilling plane can be approached.

(5) Finally, with reference to fault structures, it is suggested that the reasons why some strike faults form trap structures and others do not may be at least partly explained by the attitude of the contiguous strata. Faults which are upthrown on the down-dip side tend to have a stratum contour system which deflects the oil up-dip towards the fault. The others tend to disperse the oil.

ACKNOWLEDGMENTS.

The author would like to express his thanks to Dr. G. D. Hobson, who carried out the experimental work on which this paper is based.

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THE INSTITUTE OF PETROLEUM.

THE one hundred and eighty-sixth meeting of the Institute was held at the Royal Society of Arts on Tuesday, 14th February, 1939, at six o'clock p.m. The chair was taken by the President, Lieutenant-Colonel S. J. M. AULD, O.B.E., M.C., D.Sc.

The following paper was presented and discussed :—

"Some Factors in Oil Accumulation," by Professor V. C. Illing, M.A., F.G.S. (see pp. 201–225).

DISCUSSION.

MR. T. DEWHURST welcomed the paper, first because of its quality, and secondly because there had been all too few geological papers during recent years.

It had long been the accepted view that oil migrated from relatively fine layers to coarser layers and then laterally through those coarser and more permeable media. It had also long been accepted that the buoyancy of oil in water facilitated the upward migration of oil. Nevertheless, there was all the difference in the world between those general observations, hypotheses or inferences and the extremely careful and exact scientific research on those problems which had been carried out by Professor Illing, and which on a first reading of the paper appeared to have established beyond any reasonable doubt the scientific principles underlying the migration and accumulation of oil. Subject to a further study of the paper, he accepted unreservedly the results of the experiments, and appreciated their importance as a contribution to the elucidation of a most complicated and difficult subject.

He was also in agreement with the examples given of the application of the results of the experiments to the problem of the accumulation of oil in certain structures, but of course Professor Illing was aware of one limitation in the application of those results. He had had perforce to restrict the conditions of his experiments in order to obtain precise and accurate results. He had therefore used as media certain sands, each uniform in texture and of a definite grain size. In nature the corresponding media were much more complex, they were not uniform in texture, and in most cases they were sandstones rather than sands, and as such were probably jointed and faulted. However, even in such cases Professor Illing's principles would operate. It was to be expected that such joints, fractures, and major spaces in sandstones would facilitate lateral migration and also upward migration of oil due to buoyancy.

He hoped there were geologists present who had devoted special attention to the subject-matter of the paper and who were qualified to examine very critically the validity of Professor Illing's conclusions and inferences.

THE CHAIRMAN asked how geologists visualized the condition of the oil at the period when migration was taking place. Was the oil emulsified with the carrying water, or regarded as being in coarse droplets? If the former, he thought there might be an appreciable difference in viscosity and capillarity, depending on which was the disperse phase. Was it possible that this would still further amplify the effect of choice of path in the porous strata?

MR. R. R. TWEED remarked that he had been in the industry for 30 years, and everything he had done had depended on geologists.

It had been said that 50 per cent. of the oil was left in the ground. Was it the work of the geologist or the production engineer to get that out?

MR. C. A. P. SOUTHWELL said that he welcomed Professor Illing's paper, and hoped that it would stimulate other members to prepare similar papers. It was only by

laboratory research of this nature that the fundamental principles on which large-scale production schemes were based could be investigated. He did not wish to take up any time when there were present men who were actively engaged on these problems and whose contributions would be of value. He felt, however, that the paper gave one the impression that research on this aspect of reservoir problems was rather limited and, whilst he felt sure that Professor Illing did not wish to infer this, but only to stimulate research, he thought that there was at the present time a great deal of investigation being carried out in all the spheres of oil production, but related to the local conditions.

Mr. Southwell said he wished to ask Professor Illing if he would throw further light on one point in the paper, and that was the statement that all productive oil sands contained about 15 per cent. of connate water. He would be glad if Professor Illing would indicate what amount of data this was based on, and from which oil-producing areas it had been obtained, because it occurred to him that if this were correct, there would be less water-free oil produced in the early stages of oil production from sand-fields.

Mr. P. Docksey referred to one small point in connection with Bartell's work. The main difference between Bartell's displacement pressure and the author's fore-front pressure was that Bartell measured his specifically when there was no movement. The displacement pressure is measured under static conditions, and can be used to evaluate the adhesion tension between a liquid and solid, whereas the fore-front pressure is obtained only when the surface of separation between two liquids is in motion, and is being decreased or increased in area. The forefront pressure is thus directly related to the interfacial tension between the two liquids, and not to the adhesion tensions between these liquids and the solid.

Mr. R. J. Ward wanted to know how the oil and water was injected through the sand, and whether the pressure under which it was injected had any effect on the results.

Mr. A. Wolf asked whether the author attributed considerable importance to the well-known affinity that silica had for water, and whether he regarded that as being preferential to its affinity for oil. If this were the case, pure silica sand grains would be particularly favourable bodies for the formation of superficial water sheaths through which oil globules could pass.

Mr. A. H. Taitt wrote:

I had great pleasure in listening, as a guest, to Professor Illing's paper on "Some Factors in Oil Accumulation" and to the discussion that followed. Although I cannot add materially to anything that was said, I feel that certain data that have been obtained as a result of the drilling of Cousland No. 1 in Midlothian, by the D'Arcy Exploration Company, may be of interest.

In the Cousland borehole a sandstone was cored between 1582 ft. and 1632 ft. from surface. This sandstone was tested by means of a Halliburton Full Hole Tester, which was run to various levels in it, and a total gas-production of approximately 4 million cubic feet per day was obtained, without a trace of either oil or water.

The sandstone core was impregnated with petroleum to varying degrees, but each band of impregnation was quite distinct, and there was no gradual passage from weak impregnation to strong impregnation, as the following details will show:—

1582–1605.	Light brown sandstone.
1605–1613.	Oil-soaked sandstone, oozing oil.
1613–1623.	Micaceous grey shale.
1623–1625.	Oil-soaked sandstone.
1625–1629.	Oil-soaked sandstone, oozing oil.
1629–1631.	White, well-cemented sandstone.
1631–1632.	Oil-soaked sandstone.

From a preliminary examination of the cores it was felt that the strata to 1605 ft. might be in a gas-horizon, and below that depth in an oil-horizon. Tests carried out below 1605 ft. failed, however, to obtain even a trace of oil; gas only was produced.

Samples of cores were subjected to detailed examination with interesting results, which I think to some extent provide an explanation of the phenomena recorded.

	Sample from 1582–1605 ft. horizon.	Sample from 1605–1613 ft. and 1625–1629 ft. horizons.	Sample from 1629–1631 ft. horizon.	Sample from 1631–1632 ft. horizon.
Permeability (millidarcys) . .	303	41	2	2·75
„ after extraction with benzine	327	48	—	6·98
Porosity, % . .	17	15·4	—	—
Oil by weight, % .	0·5	2·1	—	—
Water by weight, % .	2·4	2·8	—	—
Gas yield litres/kg of core . . .	1·24	4·0	—	—

These samples of cores were sealed in air-tight tins immediately on removal from the core-barrel, in order to reduce dispersal of their contents to a minimum. Unfortunately the sealed tin containing the core from the 1582–1605 ft. zone was damaged, and this fact may account to some extent for the low gas-yield.

The water contained in the cores, extracted by pulverizing the samples, was saline, and therefore, to some extent at least, original water, and not entirely contamination from the drilling fluid, which was a fresh-water-base mud.

There can be little doubt, however, that the permeability of the various horizons is the most important factor governing the nature of the impregnation.

It would seem that the strong oil-impregnation found in the less permeable, but not in the almost impermeable zone, may have been to some extent trapped residual oil.

It is to be hoped that Professor Illing will continue his experiments using fluids under pressure, and that gas will be introduced with the oil. Perhaps it may be found that the gas will select the coarser or more permeable sands, and that the oil will be compelled to take the second best, and thus an explanation may be found for the sometimes erratic incidence of oil and gas in neighbouring fields.

Reply to the Discussion by Prof. V. C. Illing.

To Mr. T. Dewhurst.

The author in reply to Mr. Dewhurst said that the experiments had been carried out with sands of limited grade size in order to simplify the conditions. Natural sands were, of course, less well graded, but the effects would be governed by the same principles. The material point was in each case the limiting size of the pores, and as these dimensions were very much dependent on the finer particles of a sand, it would be the smaller particles that would determine the forefront pressure.

Jointing, faulting, and fissuring introduced an independent set of factors which undoubtedly had important effects on oil–water movement. The author had not been able to more than touch upon the fringe of this problem.

To the Chairman.

The Chairman's query as to the state of the oil–water mixture during migration raised a very important point. At first sight it would seem obvious that the two fluids would be emulsified in their passage through the fine interspaces between the clay particles. Experiments on oil–water–clay mixtures showed that this was not the case. Most of the oil and water chose certain definite flow-lines through the clay, and reached the sand in a completely separate condition. It is, of course, possible that in the case of certain crudes emulsification might be produced in the clay before they reached the sands, but this did not appear to be the normal behaviour.

To Mr. R. R. Tweed.

In reply to Mr. Tweed, the author would not like to lay down any hard-and-fast rule as to the relative functions of the geologist and the engineer in production practice.

It must, however, be realized that efficient oil extraction depended on several inter-related but quite separate factors. There was the nature of the reservoir, the physical behaviour of oil–water–gas mixtures, and the engineering problems associated with production technique. None of these could be neglected, and few men had a complete grasp of all. Probably the best results would be attained by collaboration of the geologist and the engineer.

To Mr. C. A. P. Southwell.

Mr. Southwell had raised the question of the water content in an oil sand. In the author's experience all oil sands contained water, although none might be given up during production. This agreed with the results of physical experiments and with laboratory tests of well samples taken in such a way as to exclude drilling muds. The explanation lay mainly in the water annuli at the points of contact of the grains.

Quantitative work showed that these annuli contained about 10–20 per cent. water which could not be removed by normal flow methods. The quantity depended, not so much on the absolute grain size, as on the variation in grade size. The condition was analagous to the draining of water-saturated or oil-saturated sands. Each, when completely drained, had about 15–20 per cent. of liquid still retained in the sand. If, however, we were dealing with sands in nature, they always contained both water and oil, and the residual annuli were composite, an inner water ring with an outer oil ring. The local fluid so retained was usually about 20–25 per cent.

Such laboratory figures agreed quite well with tests of natural oil sands at Pechelbronn and elsewhere.

If a sand is orginally wetted with oil and then water is passed through, the composite annuli of oil and water usually ranges from 15 to 23 per cent, dependent on the grade size, but the results fluctuate because of a tendency of the oil and water to replace each other, the water going to the inner part of the annulus.

All these results depended more on uniform grade size than on the actual grade of the sand. The figures of oil retention might be severely changed by the pressure of dissolved gas. On this point the author had no data.

To Mr. P. Docksey.

The author agreed with Mr. Docksey that displacement pressure was not the same phenomena as forefront pressure. He had, however, felt it was better not to be too categorical on this point, as there was considerable confusion already in the use of Bartell's term.

To Mr. R. J. Ward.

In reply to Mr. Ward, the oil and water were passed into the sand at quite low pressures by arranging water current into which oil drops could be inserted at regular intervals.

To Mr. A. Wolf.

With regard to Mr. Wolf's question, the experimental results he had described could be produced in silica or limestone particles. The only important question was the primary fluid film on the grains. It is probable that, given static conditions for a considerable time, the processes of selective adsorption would take place, but this did not occur to any recognizable extent in the author's experiments.

To Mr. A. H. Taitt.

The examples described by Mr. Taitt were almost certainly cases of the same phenomena, except that gas was involved in addition to oil. Where gas occurred in association with oil, the former selected the coarser zones, and the oil was relegated to an intermediate position between the water and the gas. There were, however, other factors coming in, and the author's experiments in this direction had not as yet proceeded far enough to warrant him in reaching more than tentative conclusions.

THE ANALYSIS OF THE KEROGEN OF OIL SHALES.

By A. L. Down, A.R.C.S., B.Sc., D.I.C. (Student)

Summary.

Attention is directed to the difficulties in the determination of the correct composition of the organic matter in oil shales, due to uncertainties caused by the accompanying mineral constituents. The attempts of previous workers to isolate the kerogen are surveyed and the method adopted described. Samples of five British oil shales have been examined, and 99 per cent. of the mineral matter removed by acid treatment. The composition of the kerogens calculated from the analyses of the de-ashed samples is compared with those obtained from the ultimate analyses of the original samples.

The economic importance of oil shales and related materials depends entirely on their content of organic matter, and no substantial advance in our knowledge of their constitution can be made unless the composition of that organic matter, usually termed kerogen, can be correctly determined. Owing to the high percentage of mineral constituents present in most oil shales and their intimate association with the kerogen, the true amount of organic matter and its composition cannot easily be ascertained. Whereas the percentages of organic carbon, nitrogen, and sulphur can be estimated directly, the organic hydrogen and total mineral matter contain errors of considerable magnitude due to the unknown of amount water present in the hydrated minerals.

The percentage of hydrogen is estimated by combustion in a stream of oxygen and weighing the water thus formed; the temperature employed is approximately 800° C., at which temperature all the water present in the hydrated minerals such as clay, which is not removed by drying at 105° C., is driven off, and hence the value for the hydrogen is high, and the ash low. J. B. Robertson,[1] when analysing a number of Scottish oil shales, made an attempt to correct for the error thus incurred, his method being to heat the samples to 200–250° C. in a current of dry nitrogen and collect the water driven off in a weighed calcium-chloride tube. The corrections thus obtained were small, the maximum, which were on a sample of Broxburn Main oil shale, being :—

Analysis . .	C = 24·88%, H = 3·79%, Ash = 60·84%
Corrections .	H = − 0·12%, Ash = + 1·06%

It is impossible that all the combined water in the clay and similar minerals was driven off at this low temperature, and this is clearly shown by the following figures of J. W. Mellor [2] :—

Table I.

		Losses of Water on Heating.			
		300° C.	400° C.	500° C.	600° C.
China Clay.	Vacuum . .	0·24%	0·39%	8·48%	—
	Atm. Pres. . .	0·26%	0·57%	1·19%	11·92%
Kalonite.	Vacuum . .	1·66%	1·70%	4·96%	11·58%
	Atm. Pres. . .	1·82%	1·91%	2·41%	10·08%

"The 13–14 per cent. of combined water is rapidly given off as the temperature rises above 500° C. at ordinary atmospheric pressure. It requires a high temperature to expel the last traces of water." Hence the corrections obtained by Robertson are too small, and the temperature required to drive off all the water is higher than that at which decomposition of the kerogen takes place.

Since the mineral matter is determined as ash on incineration at 800° C. plus the amount of carbon dioxide present as carbonates, the figure obtained is too low. The magnitude of the error is approximately 1 per cent. per 10 per cent. of clay; thus in the case of the typical Scottish oil shales, which contain 70–80 per cent. mineral matter, predominantly clays, the error involved is of the order of 3–5 per cent. Other uncertainties are introduced due to the changes that take place in the sulphur compounds on heating in air. Part of the sulphur present as pyrite is converted into sulphate, whilst the remainder is driven off, and part or all of the organic sulphur may be retained in the ash, depending on the associated minerals. Unless the shale is high in sulphur compounds the error will be small compared with that due to the water of hydration; thus the percentage kerogen is too high, and its oxygen content, which is obtained by difference and is "oxygen + errors," is of little value.

Since it is impossible to heat an oil shale to 800° C. without decomposing the organic matter, it is necessary to isolate the kerogen in order to obtain its correct ultimate analysis. Two possible methods are available:—

(1) Extraction of the kerogen with organic solvents.
(2) Removal of the mineral matter with inorganic acids.

The former methods were investigated first, and the whole range of likely solvents tried; in the great majority of cases the amount of material extractable with the usual solvents for petroleum was very small. Thus after extracting samples of Scottish oil shales successively with carbon disulphide and chloroform, the total extract was less than 1 per cent.[3] M. J. Gavin[4] reports that some 50 per cent. of the oil yield of a certain Colorado oil shale can be extracted with carbon disulphide or carbon tetrachloride. R. H. McKee,[5] working on a sample from Ione, California, obtained 10·98 per cent. extract with acetone and 10·16 per cent. with chloroform, both these represent over 50 per cent. of the oil yield on distillation. Recently H. R. J. Conacher[6] has cast doubts as to whether many of the oil-yielding materials occurring in the Middle Tertiary deposits in the western states of the U.S.A. are true oil shales, stating that it is an open question whether the oil obtained on retorting is not largely present in that form before distillation. It is well known from the work of C. Engler[7] and later workers that after heating samples of oil shales to 300–350° C., the percentage of soluble matter is greatly increased, but this is due to a change in the constitution. At the present time it is generally accepted that the organic matter of a true oil shale is practically insoluble in ordinary solvents.

One of the first attempts to isolate the kerogen by dissolving the mineral constituents was made by McKee and Goodwin,[8] who, by alternately treating Colorado oil shale with hydrochloric and hydrofluoric acids,

reduced the ash to 13 per cent. Franks and Goodier,[9] also working on Colorado oil shale, used similar methods, and were also unsuccessful. They concluded that although most of the mineral matter might be removed, complete separation was impossible. Furthermore, there was uncertainty and lack of evidence as to whether the kerogen was attacked by the reagents.

According to E. M. Bailey, "Oil Shales of the Lothians," 3rd edition, article written in 1925, M. J. Gavin had given permission to state that the isolation of the kerogen had been successfully accomplished. "The mineral constituents of the finely ground shale were dissolved away by successive very protracted treatments with very dilute reagents at a comparatively low temperature, never exceeding 100° C. That the kerogen itself was not attacked or altered was proved by the frequent determinations of the carbon–hydrogen ratio at various stages of the treatment—this ratio being found to remain constant throughout the entire process." In view of the fact that oil shales contain considerable quantities of clay and other hydrated minerals, the carbon–hydrogen ratio is bound to increase when the mineral matter is removed.

A method for concentrating the kerogen is given in a recent paper by A. J. Carlson;[10] samples of oil shales from Soldier Summit, Utah, and Montgomery County, Kentucky, were treated, and their mineral content was reduced to 7·2 per cent. and 7·4 per cent., respectively; no quantitative tests were carried out to determine whether the organic matter had been affected. R. Thiessen [11] removed most of the mineral matter from samples of Devonian shales from Illinois, Indiana, and Kentucky, and a sample of Scotch oil shale with a mixture of hydrochloric and hydrofluoric acids. Here again no mention is made of any chemical analysis of the products.

Experimental.

It was decided to endeavour to isolate the organic matter from samples of a number of British oil shales, and compare the analysis of the products with those calculated for the kerogen from the ultimate analysis of the original shales. The following samples have been examined:—

Kimeridge Oil Shale, Dorset, England.
Broxburn Main Oil Shale, Hopetown, Scotland.
Middle Dunnet Oil Shale, Westwood, Scotland.
Pumpherston Oil Shale, Duddington, Scotland.

The Pumpherston oil shale was divided into two samples by hand picking; one was distinguished by containing much crystalline mineral matter and an irregular fracture, whilst the other showed no crystals and had a conchoidal fracture. The samples were crushed and quartered, and approximately 1 kilogramme of each ground until passing a 90-mesh sieve.

The proximate and ultimate analysis, the distribution of sulphur, and the ash analysis were determined by the standard methods applied to coals. (Methods in "Fuel Testing," by G. W. Himus, 1932.)

TABLE II.

Proximate Analysis.

(Air-dried samples.)

	Ash, %.	Moisture, %.	Volatile Matter, %.	"Fixed Carbon," %.
Kimeridge . .	36·0	4·0	44·9	14·1
Broxburn Main . .	66·15	1·85	28·15	3·85
Middle Dunnet . .	75·6	2·55	18·5	3·35
Pumpherston, 1 . .	73·4	2·1	19·2	5·3
Pumpherston, 2 . .	65·3	1·5	27·3	5·9

Volatile matter determined at 900° C. by the "Bone-and-Silver" method.

TABLE III.

Ultimate Analysis.

(Samples dried at 105° C.)

	Organic Matter.					Mineral Matter.	
	C, %.	H, %.	N, %.	S, %.	O, %.	Ash, %.	CO_2, %.
Kimeridge . .	40·80	4·34	0·83	5·00	10·6	37·8	0·63
Broxburn Main . .	20·90	2·98	0·63	0·05	2·7	67·4	5·33
Middle Dunnet . .	12·98	2·04	0·66	0·22	3·2	77·6	3·26
Pumpherston, 1. .	14·55	2·05	0·92	0·05	2·7	75·0	4·70
Pumpherston, 2. .	10·02	1·60	0·60	0·03	4·0	66·3	17·45

Carbon is total carbon less that present as carbonates.
Sulphur is total sulphur less that present as sulphate and pyrite.
Oxygen obtained by difference.

TABLE IV.

Ash Analysis.

	Kimeridge, %.	Broxburn Main, %.	Middle Dunnet, %.	Pumpherston, 1 %.	Pumpherston 2, %.
SiO_2 . .	54·11	49·85	56·60	57·57	39·20
TiO_2 . .	0·85	1·29	1·25	1·43	0·97
Al_2O_3 . .	18·24	28·89	25·44	26·62	18·24
Fe_2O_3 . .	9·52	9·82	8·20	6·50	11·09
CaO . .	6·61	1·73	2·72	3·68	19·63
MgO . .	1·31	1·38	2·80	2·23	7·65
SO_3 . .	3·42	1·07	1·62	1·54	1·41
Total .	94·06	94·03	98·63	99·57	98·19

The removal of the mineral matter was then attempted by the following three-stage treatment:—

(1) Heating the sample suspended in 5*N*-hydrochloric acid on a steam-bath for 2 hours. This treatment dissolved calcium, magnesium and iron carbonates, sulphates and a small amount of silica. The residue was thoroughly washed, dried, and weighed; the filtrate and washings were

analysed and a weight balance was obtained. (The percentage of carbon dioxide evolved from the carbonates was determined in a separate experiment.) In every case the total mineral matter found in the solution agreed very closely with the decrease in weight of the sample.

(2) Iron pyrites was extracted by allowing the product to be in intimate contact with nitric acid, sp. gr. 1·12, for 100 hours at room temperature. For the Scottish samples the percentage residue plus the iron and sulphur present in the resulting solution equalled, within the limits of the experimental errors, the amount of material treated. With the Kimeridge oil shale, however, a gain in weight was observed. Determinations of the nitrogen content were made; this was found to have increased, and calculations showed that the increase in weight of the kerogen could be accounted for by assuming that all the additional nitrogen was present as NO_2 groups. Hence for this oil shale the nitric-acid treatment was omitted and the de-ashing carried on without removal of the pyrites.

(3) The residue was made into a paste with 5*N*-hydrochloric acid, and the silicates were attacked with hydrofluoric acid, the operation being carried out in a platinum dish. When no further action was apparent in the cold the vessel was gently heated on a steam-bath and the liquid slowly evaporated. The solid mass was broken up, finely ground, and then boiled with a strong solution of sodium carbonate, to decompose insoluble fluorides, filtered and washed, boiled with a large volume of dilute hydrochloric acid, again filtered and thoroughly washed. The product was returned to the platinum dish and the whole process repeated, using a considerable excess of hydrofluoric acid. Finally the residue was dried and weighed.

The samples of the de-ashed oil shales were then analysed; carbon and hydrogen determined by combustion in a stream of oxygen, nitrogen by Kjeldahl method, sulphur by Eschka method, mineral matter by incineration at 800° C., and oxygen by difference. From the analyses it can be seen that in no case was the kerogen obtained entirely free from mineral matter, although the ash was only of the order of 1–2 per cent., representing not more than 0·5–1 per cent. of the original mineral content. The ash from the Kimeridge sample, 2·16 per cent., was practically pure ferric oxide, and the amount corresponded closely with that which would be left on incineration of the pyrites in the shale. The amount of inorganic sulphur remaining was therefore determined and found to be 1·76 per cent.; if all the iron—*i.e.*, 1·57 per cent.—was present as pyrites, FeS_2, the corresponding percentage of sulphur would be 1·73 per cent. Thus it was concluded that the mineral matter in the de-ashed Kimeridge sample was 3·32 per cent. of iron pyrites. The value for total sulphur obtained was 10·30 per cent., which therefore consisted of 8·54 per cent. organic sulphur and 1·76 per cent. pyritic sulphur.

For the Scottish samples only very small quantities of the ashes were available, and complete analysis could not be undertaken. Their colour varied from white to pale yellow, and they contained over 50 per cent. silica. It was apparent that they were in a very fine state of subdivision, and may have been protected from the action of the acids by being completely surrounded by organic matter. It might be possible, therefore, to remove all the mineral matter from a sample that was sufficiently finely ground.

TABLE V.

Analysis of De-Ashed Samples.

	C, %.	H, %.	N, %.	S, %.	O, %.	Mineral Matter, %.
Kimeridge . . .	66·68	6·87	1·34	8·54	13·25	3·32
Broxburn Main . .	79·33	8·56	2·29	0·10	8·38	1·34
Middle Dunnet . .	77·83	8·09	2·62	1·22	9·22	1·02
Pumpherston, 1 . .	79·13	7·56	2·27	0·60	9·32	1·12
Pumpherston, 2 . .	77·42	8·30	3·12	0·46	9·33	1·37

The composition of the kerogen was calculated from the analysis of the de-ashed samples and compared with that obtained from the ultimate analysis of the original oil shales. In the former series of figures, since the percentage of mineral matter is very low, calculation to 100 per cent. organic matter cannot involve any appreciable error. The oxygen, being obtained by difference, still contains the algebraic sum of the errors from the other determinations, but, even so, should approximate closely to the true values.

Considering the two series of analysis for the four samples of Scottish oil shales, the most striking point is the difference in the oxygen values. The oxygen contents as calculated from the original analysis, in which the large errors previously mentioned were involved, vary from 10·3 per cent. on the Broxburn to 25·3 per cent. on the Pumpherston 2 (Table VI., p. 236). On the other hand, the values from the de-ashed samples range only from 8·58 per cent. to 9·4 per cent. There is consequently a great change in the carbon–oxygen ratio; they are higher, and instead of ranging from 2·4 to 7·3, all fall within the limits 8·3 and 9·4.

The percentages of carbon are higher, whilst the percentages of hydrogen are lower, thus causing a considerable increase in the carbon–hydrogen ratio.

Comparing the compositions of the kerogens of the Scottish shales, occurring in the Lower Carboniferous strata, with the Kimeridge shale, of Jurassic age, the carbon–hydrogen ratios show no distinction, but there is a marked difference in the carbon–oxygen ratios.

The methods adopted are considered suitable for the isolation of the kerogen, and although complete separation was not obtained, the samples were sufficiently low in mineral matter to allow accurate determination of their composition.

ACKNOWLEDGEMENTS.

This paper is based on the results of one of the series of researches on oil shales and related materials at present being carried out in the Fuel Laboratories of the Imperial College of Science and Technology, London, under the supervision of Dr. G. W. Himus, who initiated the work. The author wishes to express his thanks to Dr. Himus for his interest in the work and many helpful suggestions and for permission to publish this paper.

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TABLE VI.

Compositions of the Kerogens.

	Kimeridge.		Broxburn Main.		Middle Dunnet.		Pumpherston, 1.		Pumpherston, 2.	
	Calculated from Analysis of Dry Oil Shale. %.	Calculated from Analysis of De-ashed Sample. %.	Calculated from Analysis of Dry Oil Shale. %.	Calculated from Analysis of De-ashed Sample. %.	Calculated from Analysis of Dry Oil Shale. %.	Calculated from Analysis of De-ashed Sample. %.	Calculated from Analysis of Dry Oil Shale. %.	Calculated from Analysis of De-ashed Sample. %.	Calculated from Analysis of Dry Oil Shale. %.	Calculated from Analysis of De-ashed Sample. %.
Carbon . .	66·25	68·98	76·3	80·41	67·8	78·63	71·7	80·02	61·1	78·49
Hydrogen .	7·05	7·10	10·9	8·67	10·6	8·17	10·1	7·65	9·7	8·41
Nitrogen . .	1·35	1·38	2·3	2·32	3·4	2·65	4·5	2·30	3·7	3·16
Sulphur . .	8·1	8·83	0·2	0·10	1·2	1·23	0·2	0·61	0·2	0·47
Oxygen . .	17·25	13·71	10·3	8·58	17·0	9·32	13·5	9·42	25·3	9·49
Total .	100·0	100·00	100·0	100·00	100·0	100·00	100·0	100·00	100·0	100·00
C/H Ratio .	9·4	9·7	7·0	9·2	6·4	9·6	7·1	10·4	6·3	9·3
C/O Ratio. .	3·8	4·3	7·3	9·4	4·0	8·5	5·3	8·5	2·4	8·3

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TRANSITION EFFECTS IN PARAFFIN WAX.

By C. R. Scott-Harley.*

Summary.

The development of a rapid and simplified method for the determination of solidification and transition points in technical and commercial products is described.

The interpretation of the results revealed by a differential cooling curve derived from commercial waxes is discussed.

It is suggested that blending waxes to give no transition point will enhance their mechanical stability over a greater range of temperature.

The disappearance of the transition point and its implications on practical problems are illustrated and discussed.

Published records of the principal investigations concerning the transition points of pure paraffins, as well as technical and commercial waxes, have been collected.

Published Investigations on Pure Hydrocarbons.

During the last ten years it has been demonstrated frequently that pure normal aliphatic hydrocarbons undergo one or more definite crystallographic changes at various temperatures below their melting points. These internal alterations in the crystal structure are usually, amongst other things, accompanied by a change in density and the release of sufficient energy to cause a change in temperature. The temperature at which this change occurs is commonly termed the transition point. The phenomenon has been studied in considerable detail by means of X-rays, and also by suitable optical observations by numerous investigators (Refs. 1–12).

Published Records on Commercial Waxes.

With regard to commercial and technical products, with which this paper is principally concerned, such waxes consist of complex mixtures of normal paraffins and other types of hydrocarbons. It appears that J. A. Carpenter [13] first showed that such waxes exhibit transition phenomena similar to those associated with pure hydrocarbons at temperatures some 10–15° C. below their melting points. His interesting results were obtained by methods, such as solubility, expansion, and density, which have so far not been applied to the pure compounds. On the other hand, attempts have been made to examine commercial paraffin waxes by means of X-rays. Piper, Brown, and Dyment [2] found that a crude paraffin wax showed the same spacings as the hydrocarbon n-$C_{28}H_{58}$. Later, G. L. Clark [12] showed the apparent relationship between the melting point of commercial waxes and the corresponding pure hydrocarbons as deduced from the X-ray diagrams. Subsequently, Yannaquis [8, 9] investigated, by means of X-rays, some technical waxes derived from the vacuum fractionation of commercial 52° C. M.P. wax, and also determined the transition points by observation

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under a microscope provided with a heating stage. The conclusions advanced on the basis of the crystallographic data of these specimens have been criticized by the present author in the discussion of a paper by P. G. Higgs,[14] which was subsequently illustrated.[15] The same viewpoint has been confirmed and amplified recently in an excellent paper by Kolvoort,[11] who describes transition phases of pure hydrocarbons.

Observations of a New Character.

If the study of wax is limited to microscopic slides, it is extremely doubtful whether all the phenomena associated with crystallization can be observed. For instance, a thin film of wax under a cover-glass is usually held so tenaciously that it is impossible to detect at what temperature during cooling air is absorbed by the wax, if at all. It has been found convenient to make small cuvettes with 2-in. × 1-in. microscope slides, separated about the thickness of a cover glass, and sealed with synthetic resin on three sides only. The gap is sufficient to permit insertion of a fine-gauge thermocouple connected to a reflecting galvanometer. The cuvette is recessed between two water-cells mounted on the microscope stage and connected to a suitable thermostat. Using a calibrated thermocouple in the wax itself and thermometers in the water-stream, there is no difficulty in determining the temperature of the specimen. With ordinary wax, it is comparatively easy to observe during cooling :

(1) That an appreciable quantity of wax remains as an isotropic viscous fluid some degrees below the so-called melting or setting point.

(2) That contraction does not commence until a later stage of cooling; it appears to coincide with the temperature at which air is seen to enter the wax. This point probably represents the final solidification.

(3) That at a still lower temperature a transition may take place, accompanied by a volumetric change, an evolution of heat, and also the release of air, which is believed to be air actually dissolved in the wax, in contra-distinction to air which is drawn into the mass by contraction forces. If an air-free wax is used, this feature appears to be absent.

(4) That a second transition can be detected occasionally at a much lower temperature.

With a device such as that described it has been possible to observe an unsuspected phenomenon—viz., that in some instances a portion of wax actually liquefies and recrystallizes long after it appears to be solid. A sample, derived from a pressable wax distillate, had the following characteristics : M.P., 52° C. ; transition point, absent ; refractive index at 60° C., 1·4364. Observation was made throughout the whole crystallization, lasting 1½ hours. Immediately prior to the first crystals appearing the mobile liquid assumed a " set " condition with an anomalous viscosity over a range of 1·5–2·0° C. A definite orientation appears to exist, somewhat similar to liquid crystals, and it would be interesting to know

to what extent this phase may determine the ultimate crystal structure. Müller [7] indicates hexagonal symmetry just above the melting point for certain pure hydrocarbons. After the mass had apparently solidified, needle crystals could be observed extending from the top surface of the wax (in contact with the atmosphere). At a temperature of 43–44° C. these crystals collapsed to form another viscous liquid which became perfectly mobile at 40° C. The evidence of fluidity was readily confirmed by moving the thermocouple slightly. At a temperature of 34–35° the needle crystals reappeared. The actual quantity of wax involved in this change may be small and definite, but it is spread throughout the whole mass, and the temperature range is quite appreciable. It should be pointed out that this partial liquefaction is not common to all waxes, and the phenomenon has not as yet been associated with transition effects.

Development of Simplified Apparatus.

As a result of these observations, attempts were made to discover whether thermal analysis would indicate these changes without the use of elaborate apparatus. For the purpose of developing an extended cooling curve, two important variables—rate of cooling and quantity—were explored before the following procedure—which, of course, is quite arbitrary—was adopted.

A constant weight of wax in each operation is employed, since the values obtained are a function of this quantity. In order to transmit the effect of any changes as rapidly as possible and to minimize the temperature lag caused by the low conductivity of the solidified wax, the quantity of the sample employed is no more than that which is sufficient to cover completely the bulb of the thermometer. The requirements are most conveniently met by using 0·6 g. of wax in a test-tube 3 in. × $\frac{3}{8}$ in., and this quantity has been adopted as a standard throughout the whole of this work, except where otherwise stated. The thermometer employed is graduated in $\frac{1}{10}$° C. from 0 to 100° C. over a length of 250 mm., and the bulb is approximately 4·8 mm. × 16 mm. The wax having been melted over a water-bath, and the thermometer fixed in the tube, the latter is placed in another test-tube approximately 3$\frac{1}{2}$ in. × $\frac{5}{8}$ in., and this again is surrounded by a second air-jacket tube measuring approximately 5 in. × 1$\frac{1}{8}$ in. The set of three tubes is immersed in a beaker containing 5 litres of water at 15·6° C. to avoid atmospheric changes.* From some 5–6° above the melting point, the temperature is taken and recorded at intervals of half a minute until about 25–30° C. is reached. The operation occupies from 10 to 20 minutes in all.

Interpretation of Cooling Curves.

By inspection of the temperature differences thus obtained it is evident that the first minimum value corresponds to the melting point; the first maximum value is believed to indicate the final solidification point. If

* Any alternative device may be adopted such that the rate of cooling during the solidification stage is approximately 2° C./Min. for commercial waxes and rather less for vacuum fractionated waxes.

the internal forces modify the crystalline structure with release of energy, a second minimum value will be found to identify the transition point, which may be said to represent the maximum rate of change from the α to the β condition. As a consequence, a second maximum value can also be found, which may for convenience be termed transition set point. It

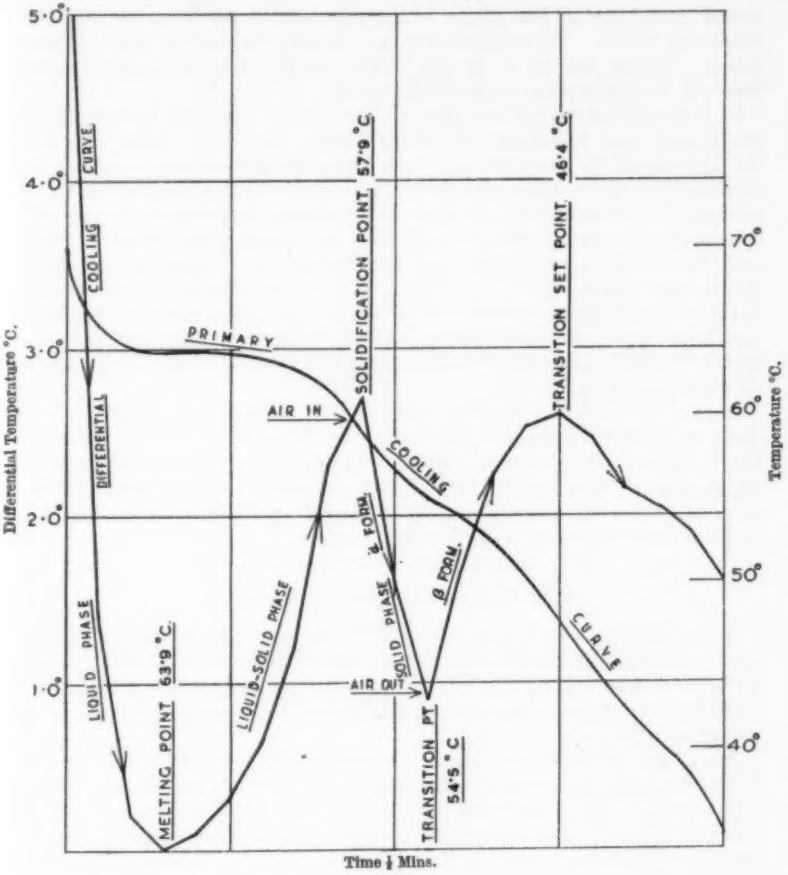

FIG. 1.

COOLING CURVE OF WAX. (78E, Table 9.)

is suggested that unless the latter point can be detected, the magnitude of the transition change is too small to be effective. The significance of these changes is seen more clearly by the use of graphs, although the latter are not essential for determination of the points. If temperatures are plotted against time, the curve shows two and sometimes three changes,

which are too indefinite to be of much value. But if the differential temperature is plotted against time, the curves show distinct maxima and minima relative to the previous inflections, which correspond to the points referred to above (Fig. 1). The general features of these curves are almost identical with those of Carpenter [13] on the coefficient of expansion of waxes. In some cases in which the heat of transition is considerable, the second minimum in the graph (T.P.) approaches the level of the first minimum (M.P.). The temperature may remain constant at both of these points. Values are given in the tables for the rate of crystallization between the melting and solidification points.

It is by no means certain that all the normal aliphatic hydrocarbons which may exist in commercial waxes possess transition points, and it is not surprising to find that in such complex mixtures as commercial paraffins the effect does not always exist in sufficient magnitude to be evident, or, alternatively, it may be smoothed out. It is found that vacuum-fractionated waxes exhibit this transition characteristic, when such does exist, very sharply and well defined, in contrast to the usual commercial grades. This is probably due to the elimination of branch-chain or cyclic hydrocarbons, which are left in the distillation residues. The latter rarely show transition changes if they are sufficiently concentrated. In this connection it is interesting to note that *iso*-paraffins show no transition point.

It has been assumed by some workers that transition is a change from plate to needle crystals or vice versa, but there is no evidence to show the occurrence of any modification whatever in the outward shape or appearance of the crystal form. This is clearly demonstrated in the excellent series of photomicrographs recently published by Kolvoort,[11] and has been confirmed by the present author.

The Effect of Rate of Cooling.

G. L. Clark,[12] using X-rays with 135° F. paraffin, has demonstrated that the rate of solidification has a profound effect on the crystalline structure, a slower rate exhibiting a greater spacing for the same wax. Yannaquis [9] confirms this finding, but does not attempt to determine its effect on transition point.

An effort has now been made to ascertain the effect of variation of rates of cooling, by using a water-bath at 35°, 60°, and 90° F. (see Fig. 2 and Table I). With relatively fast cooling rates all four points are sharp and well defined. The solidification range in the example chosen is 10·4° C. and the transition range is 8·6° C. With moderate cooling rates the solidification range is 9·6° C. and the transition range only 5·7° C. With slow cooling the solidification range is 9·5° C., but the transition phase is eliminated. In so far as the existence and magnitude of a transition change are indicative of crystalline condition, it is evident that quite a moderate change in the rate of cooling produces a pronounced effect in the body of the material. In cases in which a wax does show a transition, it is generally possible to smooth it out by imposing a sufficiently slow rate of cooling. On the other hand, it is not usually possible to bring about a transition change of any magnitude by more rapid cooling of the

wax unless it is an inherent feature of the particular sample. Other means of controlling this change are described subsequently.

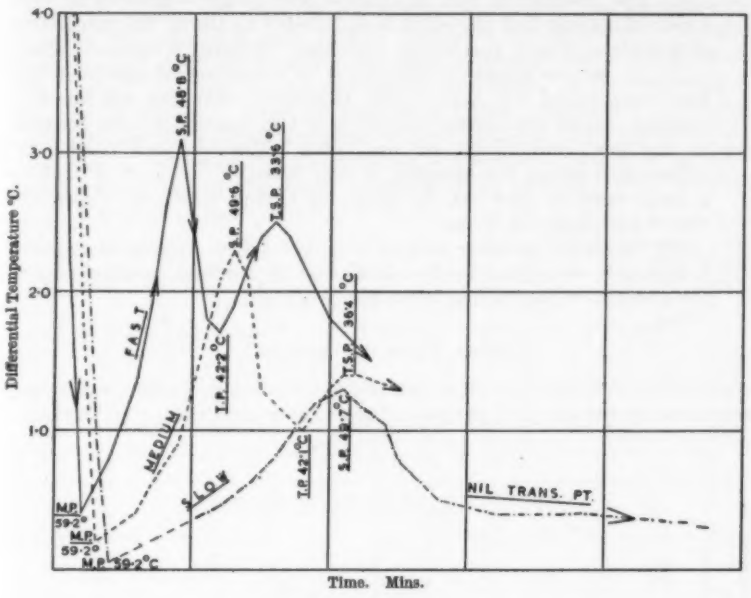

FIG. 2.

VARIATION IN COOLING RATES. (Table 1.)

TABLE I.

Effect of Variation of the Cooling Rate and Quantity of the Test Sample.

Rate.	Temp. of Water-bath, ° F.	Quantity Used in Test, gms.	Melting Point, ° C.	Solidification.		Transition Point, ° C.	Transition Set Point, ° C.	Transition Range, ° C.	Temp. Diff. M.P./T.P., ° C.	Time M.P./S.P., Min.	Rate of Crystallization, M.P./S.P., ° C./min.
				Temp., ° C.	Range, ° C.						
Fast .	35	0·6	59·2	48·8	10·4	42·2	33·6	8·6	17·0	3·5	3·00
Medium	60	0·6	59·2	49·6	9·6	42·1	36·4	5·7	17·0	5·0	1·92
Slow .	90	0·6	59·2	49·7	9·5	None	None	—	—	8·5	1·12
I.P.T. setting-point apparatus . .		14	59·3	50·5	8·8	None	None	—	—	31·5	0·28

THE EFFECT OF QUANTITY.

The procedure adopted in this work represents merely an extension of the primary cooling curve derived from determination of the setting point of commercial waxes (I.P.T. Standard Method, P.S. 11*a*) except for the quantity of material employed. Whilst it would be convenient to utilize

that method and apparatus, there are certain disadvantages in its extended use for the purpose now under discussion.

(1) The quantity of wax required—about 14 gm.—involves so slow a rate of cooling that the effect is as referred to above, the magnitude of transition, if any, practically vanishing. Stirring is impracticable.

(2) In the analogous determination of transition in metals it has been established by Ackley and Walters [16] that the temperature gradient should not exceed 0·25° C. in a 1-in. specimen. On account of the low conductivity of wax, such values as this cannot be approached unless the quantity is very small. The outer surface of a large mass of wax can be found to change its form, whilst the centre part does not do so.

(3) The large quantity employed in the I.P.T. apparatus requires 1–1½ hours, as against 10–20 minutes by the method specified above, for a record of the cooling curve temperatures.

Ideal Rate of Cooling.

It will be realized that when two waxes of different melting points are compared by the specified procedure, the cooling rates cannot be identical,

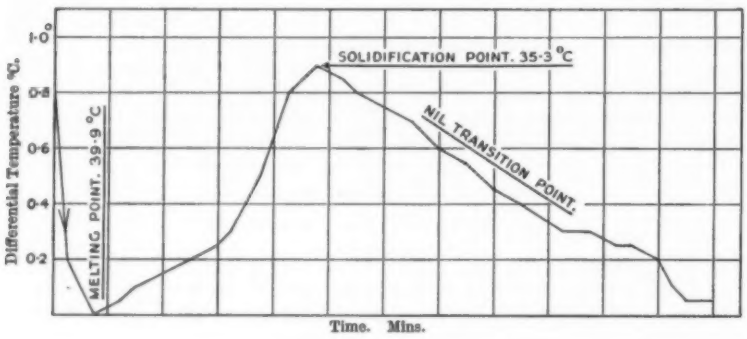

Fig. 3.

COOLING CURVE OF WAX. (80A, Table 6 and Fig. 5.)

and that even with the same paraffin the rate cannot be the same at the melting and transition points. For strict comparison it would be necessary to impose a linear rate of cooling such as that described by Skau,[17] or obtainable by means of an adjustable contact thermometer. Considering the heterogeneous nature of ordinary paraffin wax, however, the conditions suggested are regarded as satisfactory for the immediate purpose. All the transition points recorded in this paper have been determined during crystallization, largely because it is easier to duplicate the rate of cooling than the rate of heating. Results by the latter method indicate the reversibility of the phase changes, although, for obvious reasons, the values do not coincide with those observed during cooling.

As has already been stated, not all paraffins exhibit transition phenomena.

The cooling curves of two vacuum-fractionated waxes are shown in Figs. 3 and 4. 80A shows no transition point, whilst 80B has a transition phase of definite magnitude. Photomicrographs of these two waxes illustrate a uniform crystalline structure in the former case and a dual structure in the latter (Figs. 5 and 6, mag. × 80). It should not be assumed that the single uniform structure of 80A is invariably associated with the absence of transition, nor that it can necessarily be established by imposing a slow rate of cooling. Although these two waxes have nearly the same melting point, their physical properties are dissimilar. For instance, the homogeneous nature of the former type is associated with a far greater stability than that of the latter, which is more thermally sensitive and suffers distortion in the solid state.

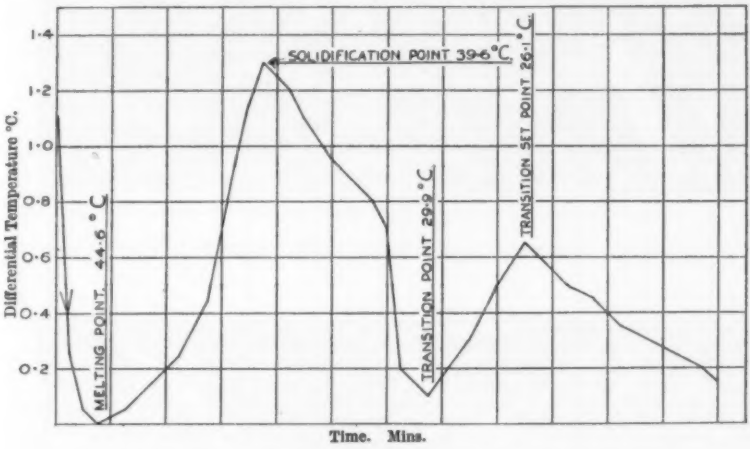

FIG. 4.

COOLING CURVE OF WAX. (80B, Table 6 and Fig. 6.)

REVIEW OF PUBLISHED DATA.

Before the results obtained with ordinary waxes are discussed, it is desirable to examine some of the records which have been obtained by previous workers with pure aliphatic hydrocarbons. The following table has been extracted from the extensive work of S. H. Piper and others,[3] in which the transition points were determined by optical means.

The relationship of melting point and transition point with the number of carbon atoms is illustrated in Fig. 7, which shows that both sets of values fall on a smooth curve and that there is a definite convergence between the melting and transition points as the length of the hydrocarbon chain increases. Müller's [7] value of 56·9° C. for the transition point of C_{29} and Garner's [10] value of 59° C. for C_{30} appear to fit the curve rather better. Garner also records the heat of crystallization and transition for five hydrocarbons. It is evident that the heat released is considerable, and usually more than half the amount evolved at the melting point.

TABLE II.

Pure Normal Hydrocarbons.

Sample.	First Transition Point on Heating (Mean Values), ° C.	Second Transition Point on Heating (Mean Values), ° C.	Melting Point (Mean Values), ° C.	Setting Point, ° C.	First Transition Point on Cooling, ° C.	Second Transition Point on Cooling, ° C.	Difference M.P./ Second T.P. Cooling, ° C.
$C_{26}H_{54}$ . .	51·75	56·0	56·5	56·1	55·5	48·3	8·2
$C_{27}H_{56}$ . .	52·9	58·85	59·05	58·5	58·0	51·0	8·05
$C_{28}H_{58}$ . .	57·2	61·2	61·45	61·1	60·4	54·0	7·45
$C_{29}H_{60}$ . .	57·4	63·2	63·5	63·2	62·2	55·8	7·7
$C_{30}H_{62}$ . .	59·25	65·15	65·7	65·4	64·3	58·0	7·7
$C_{31}H_{64}$ . .	62·25	67·3	67·7	67·3	66·2	61·8	5·9
$C_{32}H_{66}$ . .	65·3	69·3	69·6	69·2	68·6	63·9	5·7
$C_{34}H_{70}$ . .	69·3	72·2	72·7	72·4	71·4	68·5	4·2
$C_{35}H_{72}$ . .	71·9	74·0	74·5	74·1	73·0	70·5	4·0
$C_{36}H_{74}$ . .	74·0	75·2	75·8	75·6	74·6	72·5	3·3

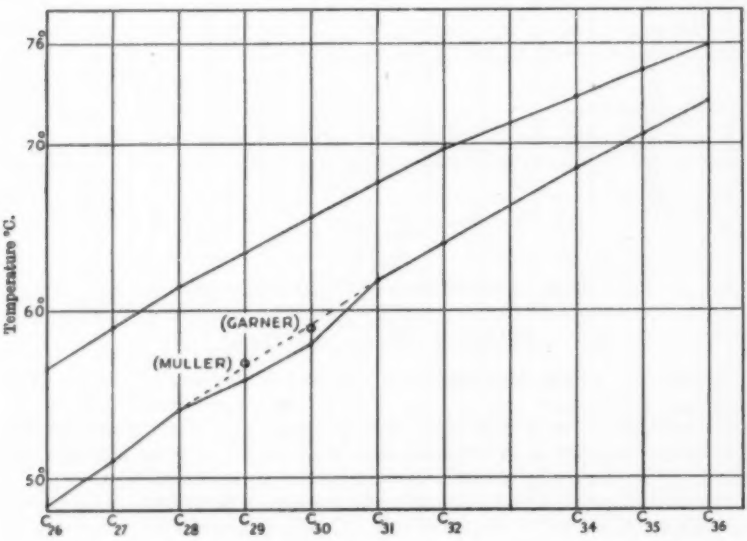

FIG. 7.

MELTING AND TRANSITION POINTS.

PURE ALIPHATIC HYDROCARBONS. (S. H. Piper and others). (Table 2.)

The next table is taken from Müller's [7] elaborate work on similar hydrocarbons with X-rays.

FIG. 5.

PARAFFIN WAX. NO. 80A. NIL TRANSITION. (× 80.)

FIG. 6.

PARAFFIN WAX. NO. 80B. TRANSITION 30° C. (× 80.)

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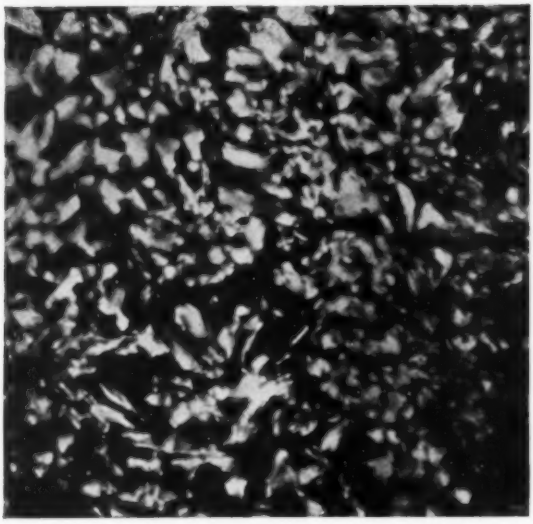

FIG. 8.

SECTION OF CANDLE WHICH STUCK FIRMLY TO THE MOULD. NO TRANSITION OBSERVED. (× 80.)

FIG. 9.

SECTION OF CANDLE WHICH DROPPED FROM THE MOULD QUITE READILY. TRANSITION CHANGE OBSERVED SOME 12° C. BELOW THE M.P. (× 80.)

TABLE III.

Pure Normal Hydrocarbons.

Sample.	Melting Point, ° C.	Transition Temperature, ° C.	Difference M.P./T.P., ° C.
$C_{24}H_{50}$ . . .	51·2	40·0–41·0	10
$C_{26}H_{54}$ . . .	58·0	45·5–46·0	12
$C_{27}H_{56}$ . . .	61·0	48·5–49·3	12
$C_{29}H_{60}$ . . .	64·4	56·7–57·1	7
$C_{30}H_{62}$ . . .	66·6	58·0–58·3	9
$C_{31}H_{64}$ . . .	68·4	60·0–64·0	6
$C_{36}H_{70}$ . . .	72·8	67·0–68·9	5
$C_{44}H_{90}$ . . .	86·4	85·6–86·0	½

The relationships observed by Piper hold good in Müller's results, and the convergence of the melting point and transition point is still more striking in the latter.

With regard to technical products, Yannaquis [9] distilled a 52–56° C. paraffin in vacuum and recorded the subsequent results of transition determined by microscopic observations.

TABLE IV.

Technical Waxes (M. Yannaquis).

Fraction.	Melting Point, Mean Values, ° C.	Transition Point, Mean Values, ° C.	Difference, M.P./T.P., ° C.
1	45·8	34·25	11·55
3	49·25	36·85	12·4
5	53·85	40·35	13·5
7	57·4	43·25	14·15
8	57·8	45·0	12·8
9	60·0 *	46·25	13·75

* This value is taken from the distillation data owing to a discrepancy in printing.

In Table IV ten fractions represent 75 per cent. and the melting-point range appears to be 17·3° C.

RESULTS AND DISCUSSION OF THE PRESENT INVESTIGATION.

The following tables present some comprehensive data obtained by differential cooling curves. Many of the transition points have been confirmed microscopically.

TABLE V.

Commercial Waxes.

	Melting Point, ° C.	Solidification Point, ° C.	Solidification Range, ° C.	Transition Point, ° C.	Transition Set Point, ° C.	Transition Range, ° C.	Temp. Diff. M.P./T.P., ° C.	Time, Mins., M.P./S.P.	Rate of Crystallization, M.P./S.P., ° C./min.
125/30 .	53·7	43·8	9·9	None	None	—	—	5·0	2·0
130/35 .	56·0	45·5	10·5	39·6	34·0	5·6	16·4	4·5	2·3
135/40 .	59·2	49·6	9·6	42·1	36·4	5·7	17·0	5·5	1·7
140/45 .	60·8	51·9	8·9	45·2	40·4	4·8	15·6	4·5	2·0

TABLE VI.

Technical Waxes.

Sample.	Melting Point, ° C.	Solidification Point, ° C.	Solidification Range, ° C.	Transition Point, ° C.	Transition Set Point, ° C.	Transition Range, ° C.	Temp. Diff. M.P./T.P.	Time, Mins., M.P./S.P.	Rate of Crystallisation, M.P./S.P., ° C./min.
80A . .	39·0	35·3	4·6	None	None	—	—	8·0	0·57
B . .	44·6	39·6	5·0	29·9	26·1	3·8	14·7	6·0	0·83
C . .	47·2	43·5	3·7	33·3	29·6	3·7	13·9	5·5	0·67
D . .	49·4	43·8	5·6	36·2	32·4	3·8	13·2	7·0	0·80
E . .	51·4	46·0	5·4	38·4	34·5	3·9	13·0	5·0	1·08
F . .	53·7	48·1	5·6	41·2	37·0	4·2	12·5	5·0	1·12
G . .	55·8	48·2	7·6	42·9	37·8	5·1	12·9	5·0	1·52
R . .	59·8	50·7	9·1	47·2	42·0	5·2	12·6	5·5	1·65

Table VI records results obtained from fractions derived by vacuum distillation of 123/5 Paraffin. Seven fractions represent 70 per cent. The melting-point range is 15·9° C.

The absence of a transition point in the first fraction has been referred to already. The depression in the transition points compared with those of pure hydrocarbons is to be expected, but the tendency to converge remains evident. Both the solidification and transition ranges tend to increase with rise in melting point. In comparison with the values obtained by Yannaquis [9] microscopically on similar melting-point wax, the data suggest that the fractionation was about the same, and that the cooling-curve method provides other information relating to the physical state.

THE EFFECT OF BLENDING ON MELTING AND TRANSITION POINTS.

Piper [3, 18] has demonstrated that whereas the melting points of binary mixtures of pure paraffins fall on a straight line joining the melting points of the components, the depression of the transition point is appreciable and tends to show a minimum. With ordinary commercial waxes the mixture law is generally applicable for melting points, but with vacuum-distilled waxes the results recorded in the following tables do not justify this generalization with regard to either the melting or the transition points. In the latter case there is considerable lowering of this value, which also tends to reach a minimum, then disappears, and finally emerges again somewhere near the original value.

In both the series forming the subjects of Tables VII and VIII two waxes have been blended together. Each exhibits a transition point.

It is conspicuous, however, that between certain percentages, different in the two series, there is no evidence of transition.

Two other waxes, respectively with and without a transition point, were blended together in a similar manner, the latter being composed of 40 per cent. 80B + 60 per cent. 80F, having a melting point of 49·7° C The results are shown in Table IX (see p. 250).

In the mixtures of wider melting points the disappearance of transition is again conspicuous, and the gap extends further with increase of melting point. It will be observed also that the solidification range increases in accordance with the range of the component melting points, and appears to be some function of the width of cut of a wax. Unfortunately, the temperature difference between the melting and transition points cannot be used as a criterion in this respect, since some waxes exhibit no transition effect at all. Nevertheless, in waxes of approximately the same melting point which do possess a transition, the temperature difference usually becomes less with increase of fractionation.

TABLE VII.

Technical Waxes.

Sample.	Melting Point, ° C.	Melting Point, Calcd., ° C.	Deviation, ° C.	Solidification Point, ° C.	Solidification Range, ° C.	Transition Point, ° C.	Transition Set Point, ° C.	Transition Range, ° C.	Temperature Difference, M.P./T.P.	Time, Mins., M.P./S.P.	Rate of Crystallisation, M.P./S.P., ° C./min.
100% 80B	44·6	—	—	39·6	5·0	29·9	26·1	3·8	14·7	6·5	0·77
90%	45·3	45·5	−0·2	40·0	5·3	26·6	24·5	2·1	18·7	7·5	0·71
80%	45·9	46·4	−0·5	39·6	6·3	25·9	24·3	1·6	20·0	8·0	0·79
70%	46·7	47·3	−0·6	39·3	7·4	28·3	22·8	3·5	20·4	8·0	0·93
60%	48·0	48·3	−0·3	39·4	8·6	27·5	25·1	2·4	20·5	8·0	1·08
50%	48·7	49·2	−0·5	39·9	8·8	None	None	—	—	7·5	1·17
40%	49·7	50·1	−0·4	40·8	8·9	None	None	—	—	7·0	1·27
30%	50·8	51·0	−0·2	41·9	8·9	None	None	—	—	6·5	1·37
20%	51·8	51·9	−0·1	43·9	7·9	33·3	31·1	2·2	18·5	5·5	1·44
10%	52·9	52·8	+0·1	44·8	8·1	37·1	33·3	3·8	15·8	5·5	1·47
100% 80F	53·7	—	—	48·1	5·6	41·2	37·0	4·2	12·5	5·0	1·12

TABLE VIII.

Technical Waxes.

Sample.	Melting Point, ° C.	Melting Point, Calcd., ° C.	Deviation, ° C.	Solidification Point, ° C.	Solidification Range, ° C.	Transition Point, ° C.	Transition Set Point, ° C.	Transition Range, ° C.	Temperature Difference, M.P./T.P.	Time, Mins., M.P./S.P.	Rate of Crystallisation, M.P./S.P., ° C./min.
100% 80B	44·6	—	—	39·6	5·0	29·9	26·1	3·8	14·7	6·5	0·77
90%	45·2	45·7	−0·5	39·3	5·9	25·5	23·7	1·8	19·7	7·0	0·84
80%	46·1	46·9	−0·8	39·3	6·8	24·6	23·2	1·4	21·5	8·0	0·85
70%	47·1	48·0	−0·9	37·9	9·2	None	None	—	—	9·0	1·02
60%	48·4	49·1	−0·7	39·9	8·5	None	None	—	—	8·0	1·06
50%	49·6	50·2	−0·7	41·5	8·0	None	None	—	—	6·5	1·23
40%	50·7	51·3	−0·6	40·9	9·8	None	None	—	—	7·5	1·31
30%	52·1	52·5	−0·4	41·2	10·9	None	None	—	—	7·5	1·45
20%	53·5	53·6	−0·1	41·0	12·5	None	None	—	—	6·5	1·92
10%	54·5	54·7	−0·2	44·7	9·8	None	None	—	—	6·0	1·63
100% 80G	55·8	—	—	48·2	7·6	42·0	37·8	5·1	12·9	5·0	1·52

TABLE IX.

Technical Waxes.

Sample.	Melting Point, ° C.	Melting Point, Calcd., ° C.	Deviation, ° C.	Solidification Point, ° C.	Solidification Range, ° C.	Transition Point, ° C.	Transition Set Point, ° C.	Transition Range, ° C.	Temperature Difference, M.P./T.P.	Time, Mins., M.P./S.P.	Rate of Crystallisation, M.P./S.P., ° C./min.
100% 80B and F	49·7	—	—	40·8	8·9	None	None	—	—	7·0	1·27
90%	50·8	51·1	−0·3	42·8	8·0	None	None	—	—	6·0	1·33
80%	51·7	52·5	−0·8	42·2	9·5	None	None	—	—	7·0	1·36
70%	53·5	54·0	−0·5	42·7	10·8	None	None	—	—	6·5	1·66
60%	54·5	55·4	−0·9	42·6	11·9	None	None	—	—	7·0	1·70
50%	56·1	56·8	−0·7	44·8	11·3	None	None	—	—	6·5	1·74
40%	57·8	58·2	−0·4	46·2	11·6	None	None	—	—	6·5	1·78
30%	59·6	59·6	Nil	48·3	11·3	None	None	—	—	7·0	1·61
20%	60·6	61·0	−0·4	52·0	8·6	49·3	40·3	9·0	11·3	5·5	1·56
10%	62·3	62·5	−0·2	55·4	6·9	52·1	48·0	4·1	10·2	5·0	1·38
100% 78E (Fig. 1)	63·9	—	—	57·9	6·0	54·5	46·4	8·1	9·4	3·0	2·00

Mixtures of two waxes having no transition exhibit similar phenomena to those illustrated above, and eventually a transition point does emerge.

It is believed that the information to be derived from any reliable method indicating the melting-point range of the principal components of a commercial wax would be of immense value in connection with the technical applications of wax. The data provided in these tables appear to be distinctly suggestive. Since when a pure substance is cooled the melting point and solidification point coincide—that is to say, the "solidification range" is nil—it is consistent to postulate that the solidification range of a mixture such as paraffin wax is an indication of the range of its constituent components. At the same time the solidification range cannot be expanded indefinitely merely by mixing together paraffins covering a long range of melting points, on account of the effect of solid solutions.

The principal deduction to be drawn from the observations of this investigation is that waxes which are blended to yield a particular melting point will be more homogeneous in structure and more stable in changing temperature if they do not exhibit a transition change. Furthermore, it seems to be distinctly probable that such waxes are likely to approach maximum values in response to mechanical tests; in this respect they may be preferred for certain uses. It is noteworthy that certain waxes possess a definite translucency, and in such cases the absence of transition is a conspicuous feature. On the other hand, waxes which are decidedly opaque are usually associated with a marked transition effect.

It is not the intention of this paper to discuss the practical applications of the transition effect, except to mention two possibilities. Waxes which are required to resist the passage of water vapour, such as waxed paper and electrical condensers, are more liable to be so resistant if they do not suffer a transition change, with consequent contraction between the crystal boundaries (Fig. 5). On the other hand, this property may be beneficial when wax is moulded. Two photomicrographs are shown, Figs. 8 and 9, (× 80) of sections of candles made with wax only. Fig. 8 illustrates the

nature of the crystalline structure when no transition effect can be observed, and in this case the candle was very difficult to remove from the mould. Fig. 9 represents a wax of similar melting point with a definite transition effect which was cooled in the same bath as the specimen above. This candle slipped out of the mould quite readily, due, it is believed, to the distinct contraction of the general crystalline structure which left fewer points of contact against the mould surface.

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KNOCK RATING OF AVIATION FUELS

THE Knock Rating Committee of the Institute of Petroleum has approved the following recommendation:—

"That the Motor Method of Test G39(T)[1] shall be employed in determining the octane number of aviation fuels with an octane number of 79 or over.

For aviation fuels below 79 octane number the employment of the Motor Method G39(T) or the Aviation Method G39a(T)[2] shall be a matter for agreement between the supplier and the consumer.

The correction specified in G39(T)[3] based on aromatic content or alcohol content shall not be applied to aviation fuels."

[1] "Standard Methods of Testing Petroleum and its Products." 3rd Edition, p. 210.
[2] *Ibid.*, p. 218.
[3] *Ibid.*, p. 215.